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14. ABSTRACT
The causes of bubbles that form when heat treating Ag-sheathed $Bi_2Sr_2CaCu_2O_8$ (2212) tapes and wires, and methods to eliminate them were studied. H_2O and CO_2, which form bubbles, are present as condensed phases in the precursor oxide powder, and O_2 is released from 2212 as it melts. Infrared spectroscopy of gases that evolved from the tape during heating showed the H_2O and CO_2 content in the tape could be significantly reduced by heating the tape at 700°C in vacuum for 24h then at 835°C for 48h in 1 atm O_2 before melt processing the tape. No bubbles formed after the H_2O and CO_2 were removed, and the tape was heated at ~1 °C/m through the 2212 melting temperature. Overpressure processing (hydrostatic pressing with a mixture of Ar and O_2) up to 10 atm total pressure could prevent bubbling but it did not remove H_2O and CO_2 from the tape. Overpressure processing could also densify the 2212 core by compressing the Ag-sheath tape during the heat treatment, eliminating the packing porosity present in the as-rolled green tape.

15. SUBJECT TERMS
BSCCO, 2212, high-temperature superconductors, bubble, overpressure processing, Ag-sheathed tape

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Final Report
Understanding the Critical current Density Limits of BiSrCaCuO High Temperature Superconductors
Grant # N00014-96-1-1115

Eric E. Hellstrom
University of Wisconsin-Madison
April 30, 2002

Summary:

This AASERT grant was used to support two women graduate students, Jodi Reeves and Nicole Scarbrough, who did research on $Bi_2Sr_2CaCu_2O_8$ (2212). Their studies, and those in the underlying main contract: showed that applying a hydrostatic pressure during the heat treatment of Ag-sheathed 2212 tapes can eliminate bubbles and densify the oxide core; identified the gases that can evolve from the oxide core and the temperatures at which they evolve; led to heat treatments to eliminate these bubble forming gases; and investigated variations in the Bi:Sr:Ca:Cu stoichiometry to reduce the size and number of grains of unreacted remnant nonsuperconducting phases in the fully processed tape. The pressure and gas evolution studies have had far reaching consequences on the processing of BSCCO tapes. The hydrostatic pressure work, which we call overpressure processing and was initiated with collaborative experiments at Hitachi in Japan, has resulted in a patent disclosure with American Superconductor to process oxide superconductors. Hydrostatic pressure processing is currently being investigated for Ag-sheathed $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ (2223) tapes. Understanding the evolution of H_2O and CO_2, the two main gases that cause bubbling, and developing methods to eliminate them during the heat treatment have markedly improved the performance of 2212 tapes and round wires. Industry is now using variations of our methods to eliminate these gases during the heat treatment. In addition, our gas evolution studies on 2212 are directly applicable to 2223 tapes.

Overpressure (OP) processing:

A recurring problem with Ag-sheathed 2212 tapes and wires is that the tape or wire can bubble during the heat treatment. Figure 1 shows bubbling in Ag-sheathed 2212 tape. Bubbling also occurs when heat treating 2223 tapes, but it is not as severe in 2223 because the processing temperatures are lower. The bubbles create gaping voids in the oxide core and distort the mechanical dimensions of the tape, rendering the tape useless. In addition to bubbles formed by gases, the as-packed 2212 powder in the green tape contains 25-35% porosity. Unless the tape or wire shrinks during the heat treatment, the resolidified 2212 core still contains at least 25-35% porosity. It was realized early on that there are two approaches to reducing the bubbling: applying a restraining pressure to prevent the evolving gas from forming bubbles or removing the source of gases that form the bubbles. The packing porosity can be removed by applying hydrostatic pressure during the heat treatment.

Figure 1 Transverse cross section of a multifilament Ag-sheathed 2212 tape showing a bubble that formed during the heat treatment. The length marker is 200µm. The original thickness of the tape was about 250µm.

Our first experiments using an applied hydrostatic pressure during heat treatment were done with Okada at Hitachi. We found that applying about 10 atm total pressure when heat treating a high C-content 2212 tape that normally bubbled prevented any bubbles from forming in the tape. However, when we subsequently reheated the processed tape at about 800C in only 1 atm total pressure, the previously flat tape bubbled severely. This confirmed that applying an external pressure prevented the gas from expanding inside the tape preventing large bubbles from forming, but it did not eliminate the gas that caused the bubbles. To truly eliminate bubbles, or a tendency to form bubbles, the source of the gas must be eliminated from the oxide core.

We built an pressure furnace at UW-Madison to continue these experiments. Overpressure (OP) is actually hot isostatic pressing, but chose to coin the term overpressure processing because (1) the total pressures we use is low (10 atm total pressure in our initial system) and (2) we use a mixture of Ar and O_2 (or N_2 and O_2), where O_2 rapidly diffuses through Ag at elevated temperature, which establishes the needed O_2 activity in the oxide core and the Ar or N_2, which cannot diffuse through the Ag sheath, applies the pressure on the tape.

Figure 2 shows the heat treatment schedule used for two tapes that had been made with oxide powder containing different amounts of C, which is present as a carbonate in the oxide core. Figure 3 shows that reducing the C content in the oxide powder and increasing the total applied pressure decreases the fraction of the tape that bubbles.

As-rolled green tape contains 25-35% packing porosity. We found that OP processing could eliminate the packing porosity, densifying the oxide core. In a related study, we found that the densification of the core depended on the physical dimensions and geometry of the Ag-sheathed tape.

Exploratory experiments to densify 2223 tapes were also done with the 10 atm OP furnace. Although the pressures were too low to densify the 2223 samples much, the concept of the OP studies on 2212 and 2223 led to a patent disclosure with American Superconductor on processing oxide superconductors with applied hydrostatic pressures. In 2001, a 200 atm system that was built for 2223 research.

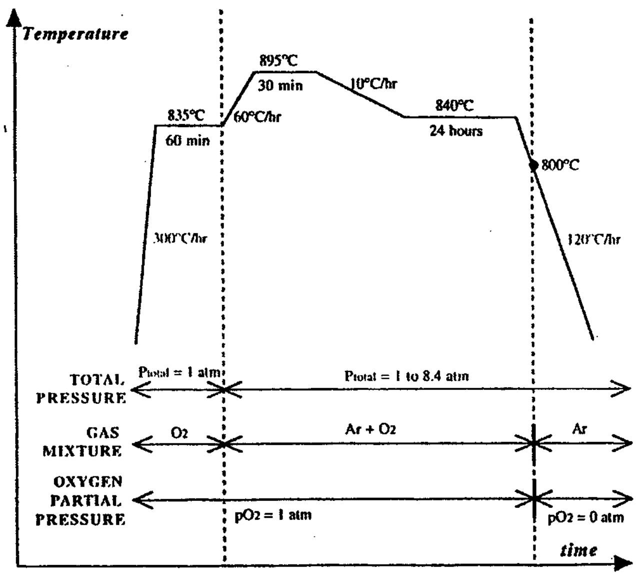

Figure 2 Heat treatment schedule used to study the effect of overpressure processing on bubbling in Ag-sheathed 2212 tapes with different carbon contents.

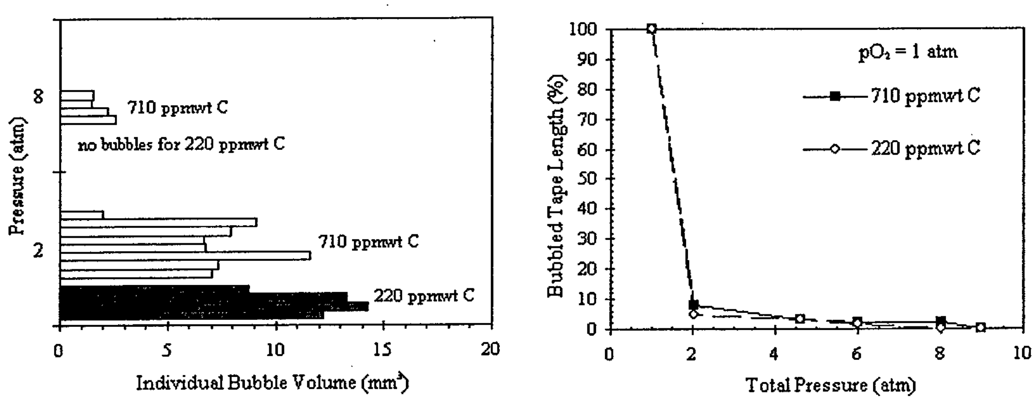

Figure 3 (a) Volume of individual bubbles that developed in tapes that contained 220 and 710 ppmwt at 2 and 8 atm total pressure ($pO_2 = 1$ atm). (b) Total bubble volume that developed as a function of total pressure in tapes that contained 220 and 710 ppmwt C.

Eliminating H_2O and CO_2 from the oxide core:

We carried out infrared spectroscopy studies to investigate the gases coming off the oxide core during heating. We suspected that H_2O and CO_2 evolved during heating, and we knew from the literature that 2212 released O_2 when it melted. Heating at about 1C/min through the melting point is slow enough that the O_2 that evolves can diffuse through the Ag sheath preventing O_2-induced bubbling.

We suspected that H_2O was present in the oxide core as H_2O adsorbed on the surface of the particles, or incorporated as crystal water in Ca or Sr hydroxides or hydrates. The CO_2 is probably present in the oxide core as a carbonate, probably $SrCO_3$ (or a mixed $(Sr,Ca)CO_3$), as $SrCO_3$ is the most thermodynamically stable carbonate. Figure 4 shows IR spectra of the gases evolved from sections of tape with and without a heat treatment designed to remove H_2O and CO_2 from the oxide core. The results show that H_2O is removed by holding the tape at 700C in vacuum for 24h. CO_2 is removed by heating the tape to 835C for 48h in pure O_2. A preheat treatment consisting of vacuum annealing at about 700C in vacuum to remove water followed by heating at about 835C in pure O_2 (at 1 atm) has been found effective for eliminating bubbles in Ag-sheathed 2212 tape. This process, or some variation on it, has been demonstrated by Oxford Scientific to prevent bubbling in >100m long section of 2212 tape.

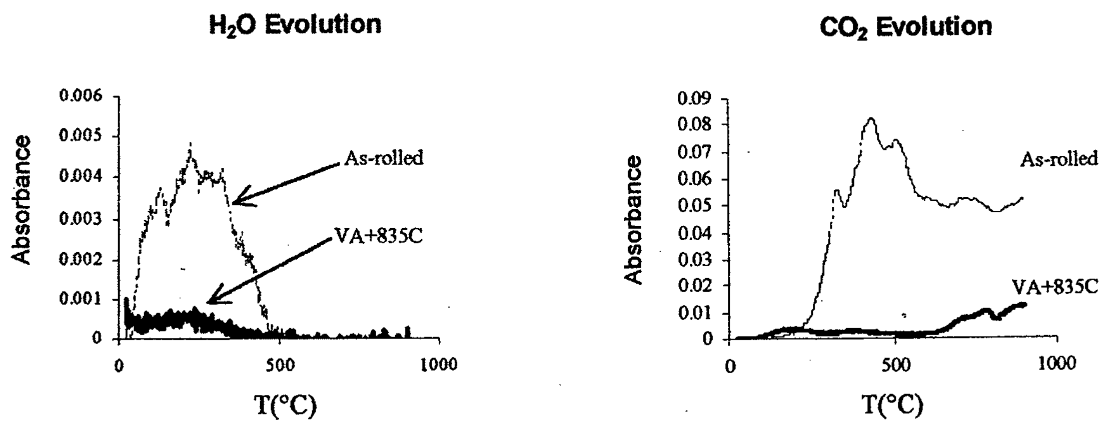

Figure 4 (a) H_2O IR absorbance spectrum showing that H_2O evolves at temperatures up to 500C from the oxide core without heat treatment. The H_2O is removed by heating at 700C in vacuum for 24h followed by 48h at 835C in 1 atm O_2 (indicated as VA + 835C). (b) CO_2 IR absorbance spectrum showing that CO_2 evolves at temperatures above 250C from the oxide core without heat treatment. Almost all the CO_2 is removed by heating at 700C in vacuum for 24h followed by 48h at 835C in 1 atm O_2 (indicated as VA + 835C).

Publications, presentations, and degrees:

The four publications listed below were supported in part by this grant. This work was presented at the meetings listed below. The 2212 studies were half of Ms. Reeves PhD studies, the other half being on $YBa_2Cu_3O_7$ coated conductors. She is now employed at IGC SuperPower. Ms Scarbrough only needs to write up her studies to finish her MS. She currently works for Ford.

Both Ms. Reeves and Scarbrough mentored several undergraduate students during her graduates studies. Some of these (D. Adolphs, A. Arndt, D. Zwicky, and V. Irizarry) are included as co-authors on the publications. Ms. Reeves also worked on 2212 tapes with Dr. B. Lehndorff, a visiting scholar from the University of Wuppertal, Germany.

Publications:

M.O. Rikel, J.L. Reeves, N.A. Scarbrough, and E.E. Hellstrom, "Effect of various processing variables on grain alignment at Bi-2212/Ag interface", Physica C 341-348 (2000) 2573-4

J. Reeves, D. Adolphs, A. Arndt, D. Zwicky, M. Rikel, and E.E. Hellstrom, "Effect of PAIR process on microstructure of Ag-sheathed Bi-2212 tapes", Physica C 341-348 (2000) 2021-2022

J.L. Reeves, E.E. Hellstrom, V. Irizarry, and B. Lehndorff, "Effects of overpressure processing on porosity in Ag-sheathed Bi-2212 multifilamentary tapes with various geometries", IEEE Trans. Appl. Supercond. 9 (1999) 1836-9

J.L. Reeves, M. Polak, W. Zhang, E.E. Hellstrom, S.E. Babcock, D.C. Larbalestier, N. Inoue, M. Okada , "Overpressure processing of Ag-sheathed Bi-2212 tapes", IEEE Trans. Appl. Supercond. 7 (1997) 1541-1543.

Presentations:

J. Reeves, Materials and Mechanisms of Superconductivity – High Temperature Superconductors VI, Houston, TX, Feb. 2000

N. Scarbrough, National Society of Black Engineers Conference, University of California-Berkeley, Apr. 1999

J. Reeves, Applied Superconductivity Conference, Palm Desert, CA, Sept. 1998