PROPERTIES OF $YBa_2Cu_3O_{7-\delta}$-Ag SUPERCONDUCTORS PREPARED BY THE CITRATE METHOD

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ABSTRACT

$YBa_2Cu_3O_{7-\delta}$ (123) ceramic superconductor and $YBa_2Cu_3O_{7-\delta}$-Ag composite superconductors have been prepared by the citrate method. Microstructural analysis has been done by X-ray diffractometry and optical ceramography. The superconducting behavior has been studied by 4-probe dc resistivity in the 77 K - 140 K temperature range. Silver percolation in the ceramic matrix was studied by electrical resistivity measurements at room temperature; the percolation threshold was found to be approximately 25 vol% (35.5 wt%) Ag. Specimens with silver addition showed improvement in the flexural strength of the 123 compound. The main results show that the critical temperature does not depend on the silver content in the composite specimens, and that approximately 3 wt% (1.8 vol%) Ag doping yields an optimized composite superconductor from the microstructural point of view, with platelet-like grain shapes.

Key words: synthesis of 123-Ag, flexural strength, electrical resistivity.

INTRODUCTION

Since the discovery of high-T_c superconductors (1) many attempts have been done to improve their properties and to overcome the intrinsic limitations of such materials for potential applications. To enhance the mechanical and electromagnetic properties, several processing methods, like melt texturing growth and chemical methods have been used (2, 3). By the same reasons the addition of different elements substitutionally or substances as second phase in the superconductor matrix has also been extensively studied (4, 5, 6).

The citrate route has been reported as a simple and efficient method for producing high quality $YBa_2Cu_3O_{7-\delta}$ (123) superconductor with better homogeneity and very fine grain size than by solid state reaction (7, 8).

The inertness and stability of silver implies no significant reaction with or degradation of the 123 superconducting properties. That metal has been pointed out as a suitable additive in the 123 matrix. Silver addition to the 123 compound is also responsible for several improvements in the superconductor's electrical, mechanical and structural properties. It has been found that silver addition improves mechanical properties (like strength and fracture toughness) (9, 10), enhances the critical current density (11, 12), reduces the normal state resistivity and improves the resistance to water (13, 14).

Effective media and percolation theories can be used for predicting physical properties, such as electrical resistivity, thermal conductivity and magnetic susceptibility of a composite media. A general effective media (GEM) equation for composite resistivity was proposed by McLachlan (15):

$$\frac{(1-f)\cdot\left(\rho_M^{1/t}-\rho_H^{1/t}\right)}{\rho_M^{1/t}+A\cdot\rho_H^{1/t}}+\frac{f\cdot\left(\rho_M^{1/t}-\rho_L^{1/t}\right)}{\rho_M^{1/t}+A\cdot\rho_L^{1/t}}=0 \qquad (1)$$

where: ρ_M, ρ_H and ρ_L are the composite resistivity, the resistivity of the high resistivity phase and the resistivity of the low resistivity phase, respectively; t is a percolation critical exponent; $A = (1 - f_C) / f_C$,and f and f_C are the volume fraction and the critical (percolation) volume fraction of low resistivity phase, respectively.

An important feature concerning the GEM equation is its validity for composites with finite electrical resistivity (conductivity) components in the full range of composition, with any spatial distribution of phases. The classical percolation theory, on the other hand, is valid only near the percolation threshold for a mixture of perfect conductors/insulators and the effective media Bruggeman's equations (symmetric and asymmetric) require special phases spatial distribution (15).

In this work the citrate method for the preparation of the superconductor composite $YBa_2Cu_3O_{7-\delta}$-p wt% Ag (hereafter named 123-Ag) with $0 \leq p \leq 50$ (0 to 37.7 vol%), its characterization by X-ray diffractometry, optical microscopy with polarized light and four-probe electrical measurements are described. A model for the Ag percolation in the 123 matrix using the GEM equation is also described.

EXPERIMENTAL

Samples with nominal silver concentration varying from 0 to 50 wt% (0 to 37.7 vol%) were prepared by the citrate method (16). The starting materials were metal nitrates: $Y(NO_3)_3$ (78%), $Ba(NO_3)_2$ (P.A.), $Cu(NO_3)_2$ (P.A.) and $AgNO_3$ (P.A.). Yttrium, barium, copper and silver nitrates were dissolved in distilled water, added together in the desired stoichiometry and mixed under heating at 60 °C. Citric acid and ethylene glycol were then added for further heating in 100 °C - 140 °C temperature baths. After approximately 5 hours a resin is obtained. Its calcination at 900 °C for 12 hours in oxygen at atmospheric pressure yields superconducting powders. The resulting powder was ground in an agate mortar and uniaxially pressed at 100 MPa into 12 mm diameter and 2 mm thickness pellets. These pellets were sintered at the same calcination conditions.

The relative concentration of silver has been determined by wavelength dispersion X-ray fluorescence spectrometry analyses in a Rigaku Denki model 3063P spectrometer. X-ray diffraction spectra of powders with different silver concentrations have been obtained at room temperature using a Philips diffractometer (PW3710) with Cu K_α radiation. Samples were polished with 15, 6, 3 and 1 μm diamond pastes for observation in an Olympus microscope (AHMT3) with reflected polarized light.

Electrical measurements were carried out by the four-probe dc method with a Hewlett Packard 4328A milliohmeter. Specimen contacts were made with silver paste. Measurements were performed in the 77 K - 140 K temperature range with 1.5 mA injected current. The sample temperature was measured with a type T thermocouple attached to the specimen. To study the silver percolation in the 123 matrix, electrical measurements were done by the four-probe dc method at room temperature.

Flexural strength of parallelepiped bars (4.7 x 7.7 x 57.8 mm^3), cold pressed at 100 MPa and sintered at the same conditions quoted above for pellets, was measured in a three-point bending mode with a support span of 25.4 mm and a crosshead speed of 0.1 mm/min in an Instron (model 1125) testing system.

RESULTS AND DISCUSSION

The X-ray diffractograms of $YBa_2Cu_3O_{7-\delta}$ powders without silver addition and with 3, 10 and 50 wt% (1.8, 6.3 and 37.7 vol%) silver are shown in Figure 1, from top to bottom, respectively. All specimens show the diffraction lines corresponding to the orthorhombic superconducting phase. The diffraction lines belonging to specimens prepared with silver show the main diffraction lines of silver (2Θ = 38.12 / 44.28 / 64.43 / 77.48).

Table I shows values of silver concentrations (as added in solution and as determined by X-ray fluorescence analysis). The largest differences are in the low added concentrations, probably due to the difficulty in collecting small amounts from the solution of silver nitrate in water. Hereafter the quoted amounts of Ag in the specimens will be the added values, i.e., 0, 3, 5, 10, 20, 30, 40 and 50 wt%.

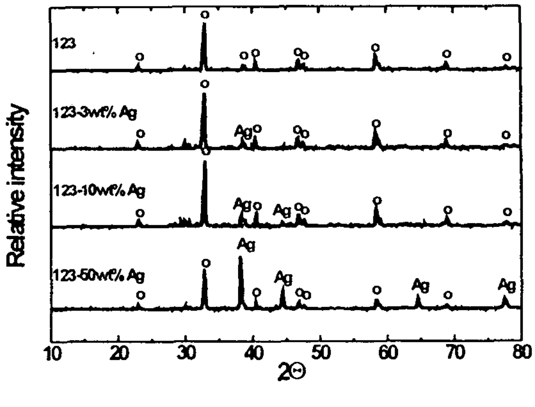


Figure 1: XRD patterns of $YBa_2Cu_3O_{7-\delta}$-p wt% (vol%) Ag for p= 0 (0), 3 (1.8), 10 (6.3) and 50 (37.7); the main diffraction lines of the orthorhombic superconducting phase are marked as "o".

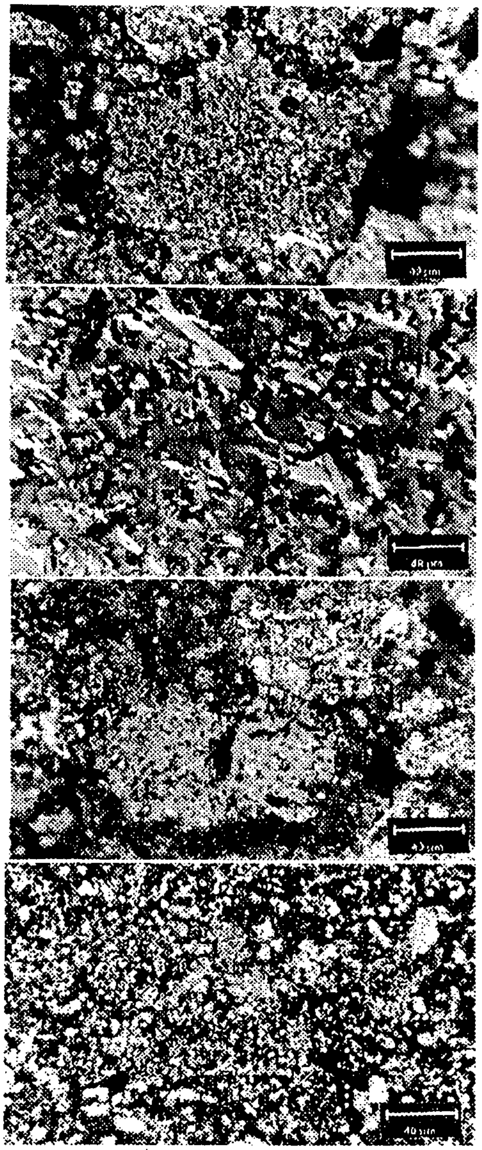
Table I: Nominal and X-ray fluorescence measured values of silver relative concentrations in 123-p wt% Ag specimens (p = 0, 3, 5, 10, 20, 30 and 50).

nominal Ag content wt%	measured Ag content wt% (vol%)
0	< 0.05 (< 0.03)
3	3.7 ± 0.1 (2.3 ± 0.1)
5	7.0 ± 0.1 (4.4 ± 0.1)
10	8.0 ± 0.1 (5.0 ± 0.1)
20	18.8 ± 0.6 (12.3 ± 0.4)
30	26.5 ± 0.1 (17.9 ± 0.1)
40	34.9 ± 0.5 (24.5 ± 0.3)
50	41.9 ± 0.7 (30.4 ± 0.4)

Figure 2 shows optical micrographs of four samples: $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ with 3, 10 and 50 wt% (1.8, 6.3 and 37.7 vol%) Ag. A special feature is observed in the micrograph of the 3 wt% (1.8 vol%) Ag specimen: platelets (roughly 24 x 4 μm^2) are formed. Silver concentrations higher than the solubility limit of that element in 123 superconductors may cause the degradation of the platelet-like morphology. These platelets could act as paths for charge carriers in the superconducting state.

Silver electrodes have been applied to the parallel surfaces of the pellets in a four contact configuration (see insert in Figure 3) for 4-probe resistance measurements. In Figure 3 resistance measurements for four specimens are shown: 123-p wt% Ag for p=0, 3, 10 and 50 (0, 1.8, 6.3 and 37.7

vol%). The resistance values have been normalized to the value measured at 140 K.



(a) (b) (c) (d)

Figure 2: Optical micrographs of $YBa_2Cu_3O_{7-\delta}$-p wt% Ag for p= 0 (a), 3 (b), 10 (c) and 50 (d). The scale bars correspond to 40μm.

Several considerations can be drawn from figure 3: the higher is the amount of silver, the more prominent is the metallic behavior of the specimens; the mid-point critical temperature, i.e., the temperature at which the derivative of the normalized resistance to the temperature reaches a maximum, is the same irrespective of the silver content in the specimens (moreover, magnetic susceptibility measurements showed the same critical temperature for those specimens); the improvement in the metallic behavior as a function of silver content shows a discontinuity for the 3 wt% (1.8 vol%) Ag specimen.

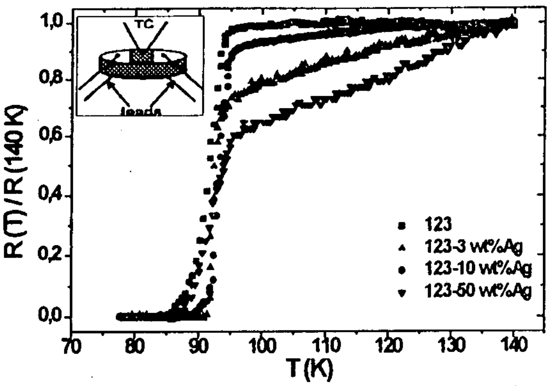


Figure 3: Electrical resistivity curves for $YBa_2Cu_3O_{7-\delta}$-p wt% (vol%) Ag composites for p = 0 (0), 3 (1.8), 10 (6.3) and 50 (37.7).

The GEM equation's fitting to the experimental data was performed minimizing the parameter δ given by:

$$\delta = [\chi^2/(N-P)]^{1/2} \qquad (2)$$

where N is the number of experimental points, P is the number of variable parameters and χ is given by:

$$\chi^2 = \sum_N [(\rho_{FIT} - \rho_{EXP})/\sigma_{EXP}]^2 \qquad (3)$$

where ρ_{FIT} was obtained by GEM equation with the XRF measured silver volume fraction, ρ_{EXP} was obtained by the four-probe dc method and σ_{EXP} was calculated by the experimental errors of the electrical resistivity and the silver concentration.

The silver resistivity used in the GEM equation was determined by the four-probe dc method using a silver pellet with the same dimensions of the 123-Ag pellets used for electrical resistivity measurements. All electrical resistivity values were normalized to the 123 electrical resistivity obtained by the four-probe measurements. The silver volume fraction was obtained from X-ray fluorescence quantitative analysis.

Figure 4 shows a good agreement between the experimental data and the GEM equation with the fitted parameters. The silver content, 27±2 vol% (38±3 wt%), for the percolation threshold is ascribed to the bad electrical connectivity between neighboring grains in the composite caused by the presence of pores and resistive phases such as Y_2BaCuO_5.

Flexural strength measurements show the enhancement of 123 flexural strength by the addition of silver (Figure 5). Improvements of the mechanical properties of 123 by the addition of silver are believed to be related to pinning of cracks by silver particles (9).

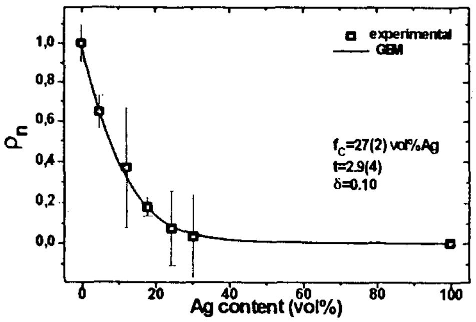


Figure 4: Normalized electrical resistivity for the $YBa_2Cu_3O_{7-\delta}$-Ag composite as a function of Ag volume fraction at 300 K. The continuous line was obtained from the GEM equation fitting.

The 123-10 wt% (6.3 vol%) Ag specimen showed about a two-fold increase with respect to pure 123, and the 3 wt% (1.8 vol%) Ag specimen has the highest flexural strength.

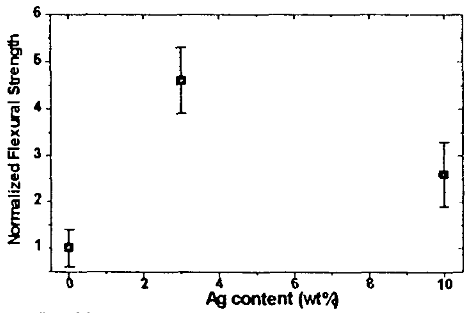


Figure 5: Normalized flexural strength values for $YBa_2Cu_3O_{7-\delta}$-p wt% (vol%) Ag for p= 0 (0), 3 (1.8) and 10 (6.3).

CONCLUSIONS

$YBa_2Cu_3O_{7-\delta}$-Ag superconducting composites have been prepared by the citrate route. The mid-point critical temperature was not affected by silver addition in the 0-50 wt% (0-37.7 vol%) composition range. The metallic behavior above T_C in the resistivity curves is improved by silver addition. The sharpness of the transitions of the resistivity as a function of absolute temperature was smoothed only above the percolation threshold, for the 50 wt% (37.7 vol%) Ag specimen. Specimens with 3 wt% (1.8 vol%) Ag showed platelet-type morphology not found in all other specimens, relatively higher flexural strength and low normal state resistivity. Grain growth in the 123-3 wt% (1.8 vol%) Ag specimen probably causes a decrease in weak-links between adjacent grains by reducing the grain boundary density. This is probably the nominal silver saturation concentration to reach the limit of the intragranular solid solubility in the $YBa_2Cu_3O_{7-\delta}$ ceramic superconductors (13).

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