Preparation and characterization of non-random YBa$_2$Cu$_3$O$_7$–Ag composite

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Abstract. Silver addition to the high T_c superconductor, YBa$_2$Cu$_3$O$_7$ (YBCO) is known to improve its mechanical properties and critical current (J_c) characteristics. We have synthesized the superconductor-metal composite YBCO–Ag by an electroless process at room temperature (using sucrose or hydrazine hydrate in an alkaline medium). The latter method produces a non-random coating whereby each grain of YBCO is coated uniformly by silver. The intrinsic high T_c of 90 K of YBCO can be recovered by compaction of the composite and subsequent heat treatment (900°C and 600°C) in oxygen.

Keywords. Silver composite; superconductor; sucrose; hydrazine.

1. Introduction

The mixed copper oxide of the formula YBa$_2$Cu$_3$O$_7$ (Y-123 or YBCO) is the well-known ceramic high temperature superconductor (HTSC) which exhibits a T_c of 90 K. In addition to the high value of T_c, it possesses other outstanding superconducting properties: upper critical magnetic field $H_{c2} \sim 150$–200 Tesla; critical current density $(J_c) \sim 10^6$ amp/cm^2 (established in thin films); low superconducting coherence length (~ 10–15 A) etc (Rao 1988, 1991). However, for practical applications at the operating liquid nitrogen temperature (77 K), the so called weak-link and flux pinning problems need to be solved to increase J_c in the bulk form. Another important challenge is to develop suitable technology to fabricate YBCO in the form of flexible wires and tapes. One way to solve the latter is to add non-interacting metallic additives like silver (Ag) to make ceramic-metal composites and extensive studies have been carried out in this direction (Peterson *et al* 1988; Peters *et al* 1988; Prasad *et al* 1988; Deslandes *et al* 1989; Dwir *et al* 1989; Miller *et al* 1989; Jin and Graebner 1991). Recently Reich and Felner (1990) reported the preparation of non-random metal superconductor composite (NRMSC) of YBCO–Ag by an electroless deposition technique and studied the physical properties including T_c behaviour. The preparative method adopted produces a non-random coating of silver (compared to the conventional mixing and grinding technique which produces a random mix or coating of the YBCO) at room temperature whereby each grain of YBCO is coated uniformly by silver. After suitable processing (oxygen treatment etc.), the HTSC properties of YBCO are regenerated with an increased J_c. However, one drawback is the formation and retention of BaCO$_3$ as an impurity phase in the YBCO–Ag composite which will degrade HTSC properties over a period of time.

Presently, we have been able to repeat the method of Reich and Felner (1990) and also used hydrazine hydrate (instead of sucrose) to prepare NRMSC–YBCO–Ag composite. The HTSC properties could be recovered after heating and oxygen treatments. The stability of the phase, resistivity and T_c behaviour have also been studied.

2. Experimental

2.1 *Sample preparation*

Well-oxygenated YBCO powder ($\sim$ 10–20 μ size; 50–100 g batch) has been prepared by vacuum calcination method (Balachandran *et al* 1989; Schartman and Hellstrom 1991; Srinivas and Subba Rao 1991). In this method stoichiometric ratio of Y_2O_3, $BaCO_3$ and CuO (all 99·9% pure) were wet-milled in acetone in a ball-mill for about 15 h. The resultant slurry was pan-dried in air, and heated at a rate of 20°C/h in the temperature range of 700–800°C in flowing O_2 at a pressure of $\sim$ 2 mm Hg and held for 4 h at 800°C. During cooling, the vacuum was discontinued and ambient pressure of O_2 was let in. A 3 h hold at 450°C was incorporated into the cooling schedule to promote oxygenation of the resulting powder. The black, free-flowing powder was then pressed into pellets and further oxygenation was carried out in a tubular furnace at 900°C, for 24 h; and then at 600°C (by furnace cooling) for 24 h, followed by slow cooling in ambient oxygen flow (by furnace shut-off). The pellets were crushed into powder and the non-random coating of Ag was carried out as follows: All the chemicals used are BDH (AR: 99·9% pure). Solution A: $AgNO_3$ (60 g/l); solution B: NH_4NO_3 (90 g/l); solution C: NaOH (105 g/l); solution D: 100 g of sucrose and 5 g tartaric acid were dissolved in 800 ml of distilled water and boiled for 15 min. After cooling, the solution was made up to 1 l with ethanol; solution E: 250 ml of 2% solution of hydrazine hydrate with 2·5 g sodium potassium tartrate was prepared in distilled water.

The required volume of solution A ($\sim$ 200 ml) was mixed with equal volume of solution B in a beaker. Then, with stirring, solution C was added to give a permanent brown tinge to the solution. The desired quantity ($\sim$ 30 g) of YBCO powder was added to the above solution and almost immediately, either 200 ml of solution D or 50 ml of solution E was added with continuous stirring. The coating of Ag occurred (and Ag mirror formation on the sides of the beaker) within 3–5 min when solution D (sucrose) was used. It was almost instantaneous when solution E (hydrazine) was used. The Ag coated powder was filtered by washing it several times with ethanol, oven-dried ($\sim$ 120°C) and then cold pressed into pellets (sizes: 25, 12 and 8 mm dia; 2–3 mm thick) using a WC-lined stainless steel die and hydraulic press ($\sim$ 4 tons). The pellets were then sintered by heating in flowing oxygen in a tubular furnace at 900°C for 24 h, and then at 600°C (by reducing the temperature) for 24 h and then slowly cooled to room temperature in the O_2 flow by the furnace shut-off.

2.2 *Characterization and measurements*

X-ray diffraction (XRD) patterns of YBCO and YBCO–Ag composites were recorded by a Rich Seifert (Germany) diffractometer with CuKα radiation. The resistivity vs temperature (77–300 K) data were measured using van der Pauw technique (both closed cycle He-refrigerator, CTI, USA or oxford cryostat (UK) with liq.N_2 and computer controlled system). The silver content in the sintered YBCO–Ag composites was estimated by gravimetric method: A known weight of composite YBCO–Ag was dissolved in 10% solution of hot HNO_3 followed by precipitation with 2 N HCl as AgCl, followed by filtering, drying and weighing. The density of the YBCO and YBCO–Ag composites were determined from the weight and dimensions of the sintered pellets.

Scanning electron micrographs (SEM) (Cambridge Stereoscan, Model 180) of YBCO and YBCO–Ag composite were taken at different magnifications to take a look at the microstructure.

3. Results and discussion

3.1 *Stability, structure and microstructure*

Since YBCO powder is sufficiently stable in basic solutions (Barns and Landise 1987), the electroless coating of Ag on YBCO powder can be conveniently carried out in basic solutions. In the above process each YBCO grain is uniformly coated by Ag metal, and when pressed into pellets and sintered at elevated temperature, results in uniform distribution of Ag-metal at the grain boundaries of YBCO. This is evident from the increase in density of YBCO–Ag composite to $5\cdot3 \pm 0\cdot1$ from $4\cdot8 \pm 0\cdot1$ g/cc for pure YBCO (theoretical X-ray density of YBCO is $6\cdot38$ g/cc).

The XRD patterns of pure YBCO and YBCO–Ag composites show the well defined orthorhombic structure for all the compounds indicating that Ag deposition and subsequent heat treatment regenerates the desired crystal structure (figure 1). The Ag-metal lines are seen in the composites prepared by both sucrose and hydrazine reduction methods. We notice slight preferred orientation (enhancement of intensities of select (001) lines) in the composite prepared by sucrose method. Most importantly, lines due to $BaCO_3$ (marked B in figure 1) are also seen in the YBCO–Ag prepared by the sucrose method. Both the above features have also been noticed by Reich and Felner (1990) during their studies. In the case of the composite prepared by the hydrazine method, no $BaCO_3$ impurities were seen; also, the intensity distribution pattern of YBCO remains almost the same as that of the starting pure YBCO material. Since hydrazine is a more powerful reducing agent compared to sucrose, it is able to affect Ag deposition instantaneously without simultaneously reducing (decomposing) part of the YBCO powder (giving rise to the corresponding decomposition products, $Cu(OH)_2$, $Ba(OH)_2$ and $Y(OH)_3$). The $Ba(OH)_2$ formed in the earlier method (sucrose) during the electroless process can lead to the formation of $BaCO_3$ by absorption of CO_2 from atmosphere. Thus, we find that hydrazine reduction method is better than sucrose method in the preparation of non-random metal superconductor composite (YBCO–Ag).

The orthorhombic lattice parameters for the pure YBCO and YBCO–Ag composites have been calculated using least square fit of the four high angle (*hkl*) reflections. Our a, b and c values for the pure YBCO, viz $a = 3\cdot82$, $b = 3\cdot88$ and $c = 11\cdot68$ Å are in excellent agreement with the literature data, thereby indicating excellent sample quality. The lattice parameters for YBCO–Ag composites do not change significantly (within experimental error) thereby indicating that Ag does not get incorporated into the crystal lattice (at the Cu-site) and acts only as a non-interfering additive to the YBCO.

The silver content in the starting solution during the electroless process was kept constant (20 wt%) for all the batches. However, there is a variation in the amount of Ag coating on YBCO from batch to batch due to the coating of Ag to the walls of the beaker. The silver content in the YBCO–Ag composite prepared by sucrose method as well as hydrazine hydrate method varied between 13–18 wt% Ag.

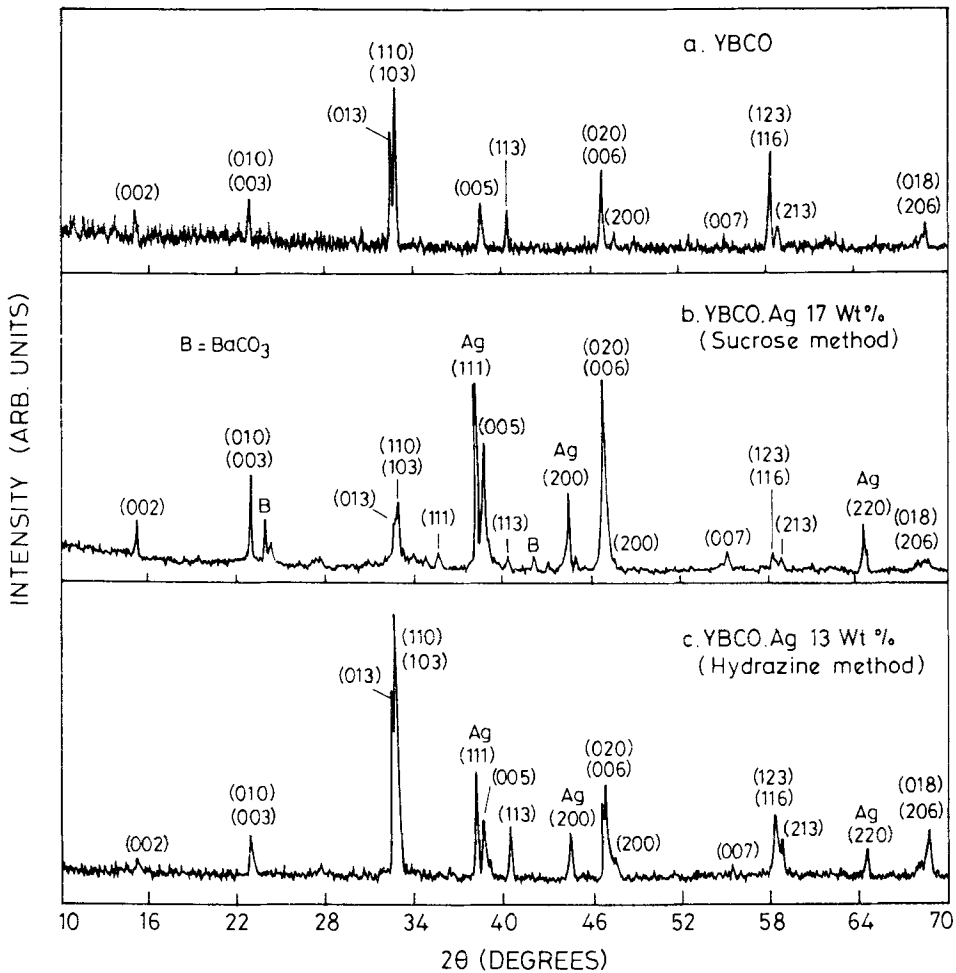The grain structure and morphology of the pure YBCO and the YBCO–Ag (17%)

Figure 1. X-ray diffraction patterns: (a) YBCO; (b) YBCO–Ag 17wt% (sucrose method); (c) YBCO–Ag 13wt% (hydrazine method). The (*hkl*) Miller indices are also shown (CuKα-radiation).

composite were examined by SEM. The pure YBCO showed a more or less uniform distribution of grains but with voids in between the grains (figure 2). The YBCO–Ag composite, on the other hand, showed a more uniform and dense structure. Thus, the Ag metal residing between the YBCO grains makes the distribution uniform. The grain size of YBCO and most of Ag metals does not change much. However, some large particle (10–20 μm size) silver grains could also be seen in some regions of the sample.

3.2 *Electrical and T_c behaviour*

DC electrical resistivity vs temperature ($\rho - T$) data on pure YBCO and YBCO–Ag composites prepared by sucrose and hydrazine methods are shown in figure 3. The ρ_{300K} values of YBCO–Ag composites are always lower than the corresponding pure YBCO. This indicates that the Ag facilitates intergrain contact between the YBCO
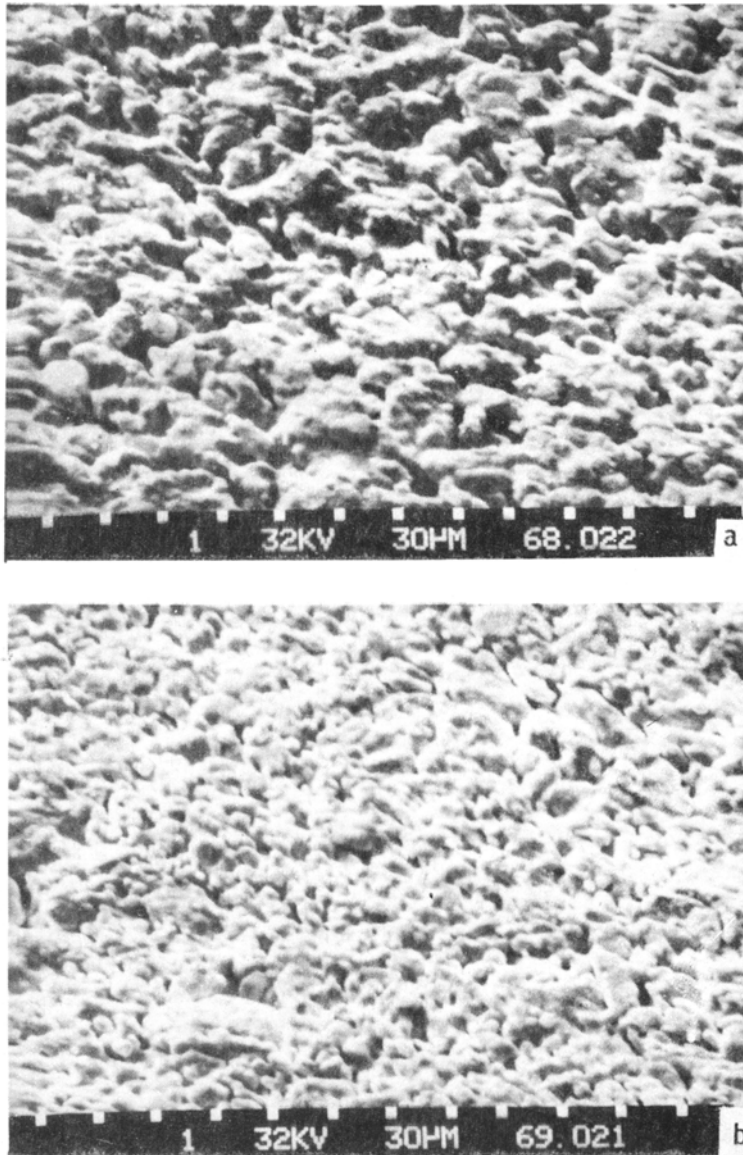
Figure 2. Scanning electron micrographs (SEM): a. YBCO(× 300) and b. YBCO–Ag 17 wt% (× 300).

grains. The linear $\rho - T$ behaviour above the superconductivity transition observed in both the pure YBCO and YBCO–Ag composites indicates the excellent quality of the sample. However, there is no perceptible change in the $T_{c, zero}$ (90 ± 1 K) as well as $T_{c, onset}$ (94 ± 1 K) for YBCO and YBCO–Ag composites. This shows that Ag does not get incorporated into the YBCO crystal lattice and only acts as a non-interactive additive. The YBCO–Ag composites are stable as can be seen from the resistivity plots (figure 3); the $T_{c, zero}$ and the room temperature resistivity values remain the same even after four months. It is also gratifying to note that $BaCO_3$ presence in the
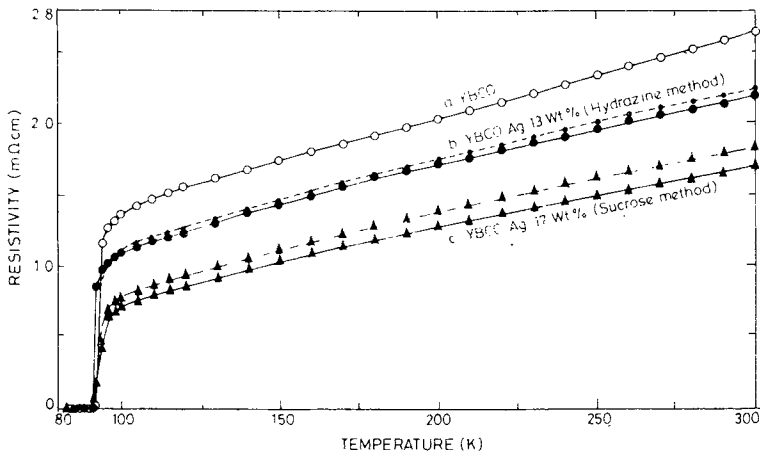
Figure 3. Resistivity vs temperature plots: (a) YBCO; (b) YBCO–Ag 13 wt% (hydrazine method); (c) YBCO–Ag 17 wt% (sucrose method). Dotted line – repeat measurement on the same sample after four months. As can be seen the T_c of 90 K is unchanged by Ag addition and the YBCO–Ag composites are stable with time.

composite prepared by the sucrose method (curve c in figure 3) does not degrade the $\rho - T$ behaviour on exposure to air/moisture at least for four months.

4. Conclusions

Non-random YBCO–Ag composites have been prepared by the electroless deposition of Ag using sucrose as well as hydrazine methods. $BaCO_3$ impurity is seen in the composite prepared by sucrose method whereas no such impurity is noticed by the one prepared by the hydrazine method showing thereby that the latter method is advantageous. Ag addition lowers the room temperature resistivity of the composite whereas the metallic behaviour and T_c remain completely unaffected indicating that Ag is acting as non-interactive additive. The composites in the form of sintered pellets are stable towards exposure to air and moisture.

Acknowledgements

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