JOURNAL OF MATERIALS SCIENCE 28 (1993) 5007–5009

Fabrication and characterization of $YBa_2Cu_3O_{7-x}$/Sn composite superconductors

Part II *Electrical properties*

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$YBa_2Cu_3O_{7-x}$/Sn (YBCO/Sn) composites sintered at 230 °C exhibited a percolation threshold for electrical conductivity at 20 vol % Sn, with semiconducting and metallic behaviour below and above it, respectively. The simultaneous decrease in $\alpha = d\rho/dT$ and ρ_0 with increase in Sn content was related to formation of defect-free interfaces. The diamagnetic shielding property of the composites weakened with Sn content, as deduced from magnetic levitation experiments.

1. Introduction

Development of bulk ceramic superconductor/metal composites is mainly aimed at improved ductility, which is essential at both the fabrication and application stages. However, choice of the metallic phase should take into account its influence on the electrical superconducting properties, i.e. its chemical compatibility with the superconductor. Recently, many investigations have shown that noble metals such as gold and silver could be used successfully in conjunction with thin film as well as with bulk superconductors [1–6], without detriment to their superconducting properties.

The present paper describes the electrical properties of $YBa_2Cu_3O_{7-x}$/Sn composites fabricated by liquid-phase sintering at 230 °C [7], and their relation to the composite microstructure.

2. Experimental Procedure

The fabrication process of $YBa_2Cu_3O_{7-x}$/Sn composites was described in detail in Part I of this paper [7]. Briefly, composite discs with 15–50 wt % Sn were prepared by liquid-phase sintering at 230 °C, and rectangular bars of 2 × 3 × 15 mm were dry-cut for d.c. resistivity measurements. These were carried out in a home-made cryostat, from room temperature down to that of liquid nitrogen (77 K), using the four-probe technique. Electrical contact with the specimens was effected by means of symmetric loading applied through the electrical printed circuits and high purity indium spheres, as shown schematically in Fig. 1. This arrangement, with the current supplied from one surface of the bar and the voltage measured on the opposite surface, minimizes the contribution of surface resistance to the measured bulk resistance. A programmable current source (Keithley model 224) and a digital multimeter (Keithley model 196) were used. The electrical resistances were measured at a constant current of 10 mA. The temperature was measured using a copper–constantan (type T) thermocouple.

The magnetic levitation behaviour of the composites in the superconducting state was studied by floating a rare-earth magnet above the specimens. Superconducting composite discs 20 mm in diameter and 4 mm thick were placed in a Petri dish and refrigerated from below with liquid nitrogen. A glass tube with inner diameter 5 mm was then vertically pressed to each disc at its centre, and the cylindrical magnet (5 mm in diameter and 8 mm in height, its pole direction parallel to its axis) was dropped into the tube through the top. The level at which the bottom surface of the magnet came to rest above the disc was measured within ± 0.2 mm, using a binocular.

3. Results

The room-temperature d.c. electrical resistivity versus Sn content is plotted in Fig. 2, which shows a significant drop in the former—by four orders of magnitude—as the content increases from 20 to 40 wt % Sn. These composite specimens could be considered as percolative systems, since the resistivities of the pure YBCO and Sn ($\sim 10^{-3}$ and $\sim 10^{-5}$ Ω cm, respectively) differ by two orders of magnitude. Thus, the percolation threshold for normal-state resistivity was found to be 22 wt % (20 vol %) Sn, at the inflection point of the curve.

The electrical resistivity of the specimens versus temperature is seen to vary with Sn content (Fig. 3). Unlike pure YBCO, composites with 15 and 20 wt % Sn showed semiconducting behaviour. By contrast, those with higher Sn contents exhibited metallic characteristics, and their resistivity curves were linear with temperature. The slopes of these curves ($\alpha = d\rho/dT$) as function of their temperature-independent term (ρ_0) at room temperature (293 K) and at 100 K (following Matthiessen's rule) are plotted on a

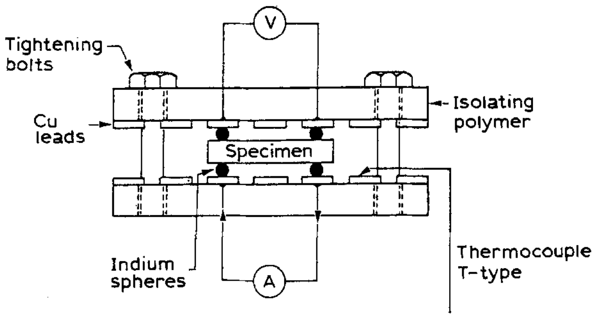

Figure 1 Schematic view of the specimen and electrical leads set-up for electrical resistivity measurements down to the liquid nitrogen temperature.

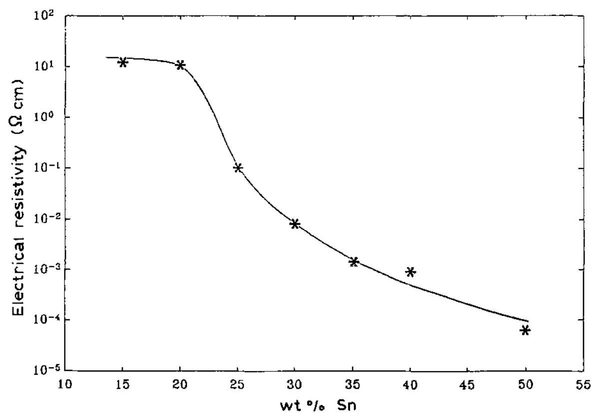

Figure 2 Room-temperature electrical resistivity of $YBa_2Cu_3O_{7-x}$/Sn composites versus Sn content.

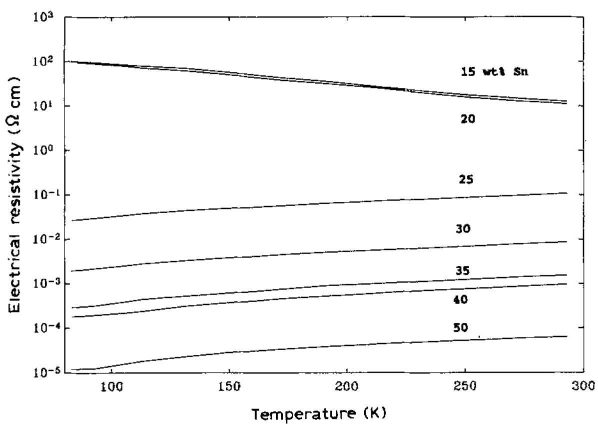

Figure 3 Electrical resistivity of the $YBa_2Cu_3O_{7-x}$/Sn composites versus temperature.

log–log scale in Fig. 4. The identical slopes of these linear plots indicate a common cause for the decrease of both parameters at the respective temperatures. No percolation threshold was observed for the superconducting phase at low Sn contents.

Relative levitation levels of the magnet at the liquid-nitrogen temperature are plotted in Fig. 5 (for two different runs), as a function of Sn content. The absolute levitation levels, as defined above, are also shown. The diamagnetic shielding property of the composites weakened exponentially with Sn content, but exponential extrapolation of the data to 100% Sn yielded a residual levitation effect of 20% compared to that of pure YBCO.

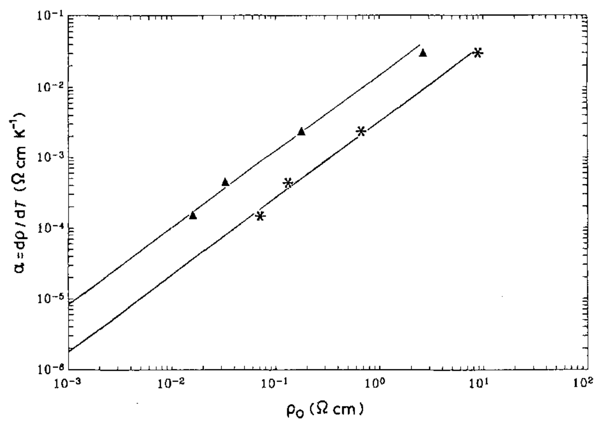

Figure 4 Thermal coefficient of electrical resistivity versus the room-temperature ($*\rho_{293\,K}$) and low-temperature ($\blacktriangle\rho_{100\,K}$) resistivities in $YBa_2Cu_3O_{7-x}$/Sn composites exhibiting metallic behaviour.

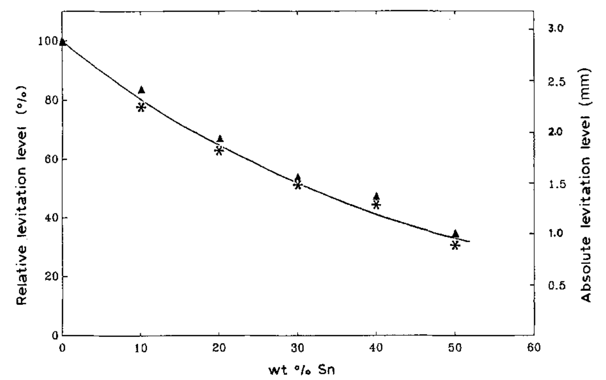

Figure 5 Relative and absolute levitation levels of the magnetic above $YBa_2Cu_3O_{7-x}$/Sn composites, versus Sn content.

4. Discussion

The steep drop in normal-state resistivity with increasing Sn content is indicative of intensified contact between Sn particles. Very similar percolation thresholds were reported for YBCO composites with gold [8] and silver [9, 10]. The observed threshold value of 20 vol % Sn could be expected for three-dimensional percolating systems.

The high resistivity of the composites with low Sn content is due to their porosity, which decreases as the metal content increases. In addition, bulk pore-free YBCO has a typical room-temperature resistivity of a few mΩ cm [11, 12], which is higher by two orders of magnitude than that of pure tin (11 μΩ cm for white tin [13]) thus contributing further to the decrease in resistance with increasing Sn content. Nevertheless, asymptotic extrapolation of the curve in Fig. 2 to 100% Sn tends to values of the order of 10^{-3} Ω cm, which is still higher by two orders of magnitude than that of pure tin. This fact indicates that in spite of the good wetting effect of the tin *vis-à-vis* the YBCO grains [14], unwetted regions remain available and provide an alternative continuous path for the electric current.

The absence of a percolation threshold for the superconducting phase indicates disappearance of the superconducting path already at very low Sn contents (below 15 vol %). The theoretical percolation threshold for both components in a random continuous medium with black and white symmetry should be around 17% [8]. This discrepancy between the observed and expected values is attributable to the morphological dissimilarity of the YBCO and Sn grains [7].

Increases in both α and ρ_0 were reported by Halbritter *et al.* [15] for polycrystalline isotropic YBCO samples with linear $\rho(T)$ dependence. The linear decrease in α with ρ_0 (Fig. 4) indicates that in composites with Sn contents above the percolation threshold, the high resistance internal contacts (at the YBCO/YBCO and YBCO/void interfaces) are gradually replaced by low resistance ones (at the YBCO/Sn interfaces) as the Sn content increases. Consequently, extrapolation of the curves in Fig. 4 down to the room-temperature resistivity of white tin (11 $\mu\Omega$ cm) yields corresponding values of α in the range 2×10^{-7} to 5×10^{-8} Ω cm K^{-1}, which is close to that for pure tin (4.47×10^{-9} Ω cm K^{-1} [14]) within an order of magnitude. Thus, the behaviour of α correlates with that of ρ_0, which decreases towards that of pure Sn, starting from the percolating composition (20 vol %).

According to the microstructural characterization of the composites (see Part I of this series), the resolution for Sn detection by EDS is comparable with its diffusion distance in YBCO (~ 2 μm) under the sintering regime, so that diffusion of Sn in YBCO cannot be determined. However, doping of YBCO with more than 10 vol % SnO at 950 °C, was reported to convert its superconductivity to semiconductivity [16]. Although our own specimens were sintered at a lower temperature (230 °C), their semiconducting behaviour may be due to the compositional changes at the YBCO grain interfaces—as well as to the presence of weak-link grain boundaries [17].

Levitation of a magnet over a flat YBCO superconductor is well documented in the literature [18–21]. In such experiments, the magnetic field should exceed the lower critical value H_{c1}, below which a full Meissner effect exists. In the present case, the magnetic field was most probably above the H_{c1} of pure YBCO (100 G at 77 K [22]), so that levitation was possible.

The levitation level was a function of the size of the magnet, consistent with other works [18–20]. No attempt was made to optimize the latter in terms of the levitation level, or to verify the force–distance hysteresis loops. However, similar levitation levels (3 mm for pure YBCO) were reported for YBCO/polymer composites [21].

The continuous drop in the levitation level with Sn content indicates a negligible effect of the diamagnetic property of tin, while that of the superconducting ceramic phase within the composite persisted below the superconducting temperature, depending on the Sn content.

Acknowledgements

The authors acknowledge the Sachs Center at the Department of Materials Engineering for providing the facilities used for this study. Partial financial support by the Fund for the Promotion of Research at the Technion is also acknowledged.

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Received 12 October 1992
and accepted 11 January 1993