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Ag distribution in thick Bi-2212 floating zone textured rods

A. Sotelo, M. Mora, M.A. Madre, J.C. Diez*, L.A. Angurel, G.F. De la Fuente

Instituto de Ciencia de Materiales de Aragón (C.S.I.C.-Universidad de Zaragoza), C/María de Luna, 3. 50018 Zaragoza, Spain

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Abstract

$Bi_2Sr_2CaCu_2O_{8+\delta}$ + *x* wt.% Ag (with *x* ranging from 0 to 40) powders were prepared by a sol–gel method. These powders were used as precursors to fabricate long textured cylindrical bars through a floating zone melting method (LFZ) induced by a continuous CO_2 laser. On the as-grown textured rods, Ag appears as spherical particles due to its low solubility into the Bi-2212 melt. After annealing, these spherical inclusions change their shape to elongated polygonal ones, which can promote better mechanical properties. This behaviour has been confirmed through flexural essays on the annealed rods. The flexural strength is about 40% higher for samples with low Ag content (<5 wt.%) than for pure Bi-2212. Furthermore, for these Ag contents, superconducting properties are nearly unchanged from the obtained values for optimised Bi-2212 LFZ textured rods. When Ag contents are higher than 5 wt.%, both the mechanical and the superconducting properties decay.

Keywords: Oxide superconductors; Superconductivity; Mechanical properties; Silver addition

1. Introduction

The development of commercial applications based on high temperature superconductors requires the use of texturing techniques in order to obtain bulk materials with the critical current densities (J_c) values that are needed for technological applications.[1] $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) superconductors have demonstrated that are suitable for many applications when they are properly processed. An example of texturing technique for Bi-2212 bulk materials is the laser floating zone (LFZ) technique.[2–4] The superconducting materials textured by this technique, have very well aligned crystals, with their *c*-axis perpendicular to the current flow direction and strong grain boundaries, obtaining J_c values higher than 5000 A/cm^2 for thick rods,[5] and with interesting properties that allows developing current leads[6] or fault current limiters[7] with these materials. One of the main advantages of this method is that the materials can be rapidly grown due to the large thermal gradient at the solid-liquid interface.[2,3] A second additional advantage is the absence of crucible, avoiding external contamination of textured samples during the processing.

However, the poor mechanical characteristics of this kind of materials,[8] due to their ceramic nature, imposes limitations for practical applications. Some attempts to improve their mechanical properties have been performed by means of Ag addition on BSCCO compounds.[9,10]

The aim of this work is to study the influence of Ag addition on the microstructure in the Bi-2212 system, if it is processed using a technique that completely melts the sample, as it is the case of the LFZ method. The changes on the microstructure are related with the superconducting and mechanical properties of the samples.

2. Experimental procedure

Bi-2212 + *x* wt.% Ag materials (*x* = 0, 1, 3, 5, 10, 20, 30 and 40) have been prepared by a sol–gel method via nitrates[11] to assure total cation solution, small particle size and good homogeneity in the mixture. This powder was thermally treated at 750 and 800 °C, for 12 h each, with an intermediate milling, to assure complete carbonate decomposition to avoid

* Corresponding author. Tel.: +34 976 76 2526; fax: +34 976 76 1957.
E-mail address: monux@unizar.es (J.C. Diez).

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bubble formation on the LFZ process. X-ray powder diffraction (XRD) analyses were performed on prereacted powders on a Rigaku EXAFS device, with 2θ between 3.5° and 60°. The reason to prepare only prereacted powders is to avoid the growth of silver particles.

These powders were used to prepare cylindrical precursors, 120 mm long and ≈3 mm diameter, by cold isostatic pressing with an applied pressure of 200 MPa. These cylinders were used as feed in a LFZ melting installation[5] to obtain textured Bi-2212/Ag composites. The obtention of textured bars was performed using a continuous CO_2 laser ($\lambda = 10.6\,\mu m$), at a growth speed of 55 mm/h, with a rotation speed of 15 rpm. After texturing, low resistance silver contacts were painted on the samples and then subjected to a two step annealing process in air (60 h at 850 °C and 12 h at 800 °C), followed by a quench to room temperature.

The V-I characteristics at 77 K of the annealed rods have been measured on 4 cm length samples by the standard four-probe configuration. The resistivity as a function of temperature was measured using a dc current of 1 mA. Mechanical characterisation was performed measuring the flexural strength, by the three-point bending test in an Instron 5565 machine with a 10 mm loading span fixture and a punch displacement speed of 30 μm/min. Microstructure of samples was determined using a JEOL 6000 SEM microscope provided with an energy dispersive spectroscopy (EDX) system.

3. Results and discussion

XRD diffraction data show that the prereacted powders are a mixture of different phases, mainly Bi-2212 and Bi-2201 with Ca_2CuO_3 (2:1), $(Sr,Ca)CuO_2$ (1:1), Cu_2O and $(Sr,Ca)_{14}Cu_{24}O_{41}$ (14:24) as secondary phases. Silver can be detected only in samples where its content is higher than 3 wt.%. The silver content strongly affects the melting process because higher is the silver content higher has to be the laser power in order to obtain similar melting conditions. It was found that, it was impossible to grow samples with Ag contents higher than 20 wt.% due to the instabilities originated for the presence of these big amounts of silver in the melt. This is a consequence of the low solubility of the Ag in the Bi-2212 melt.[12] The microstructure of the as grown samples is the typical that is obtained in these materials[4] with spherical silver particles between the Bi-2201 grains (Fig. 1a).

After texturing, the samples were annealed to obtain the Bi-2212 phase.[4] During the annealing the Bi-2212 phase becomes the main one and it can be observed that the silver

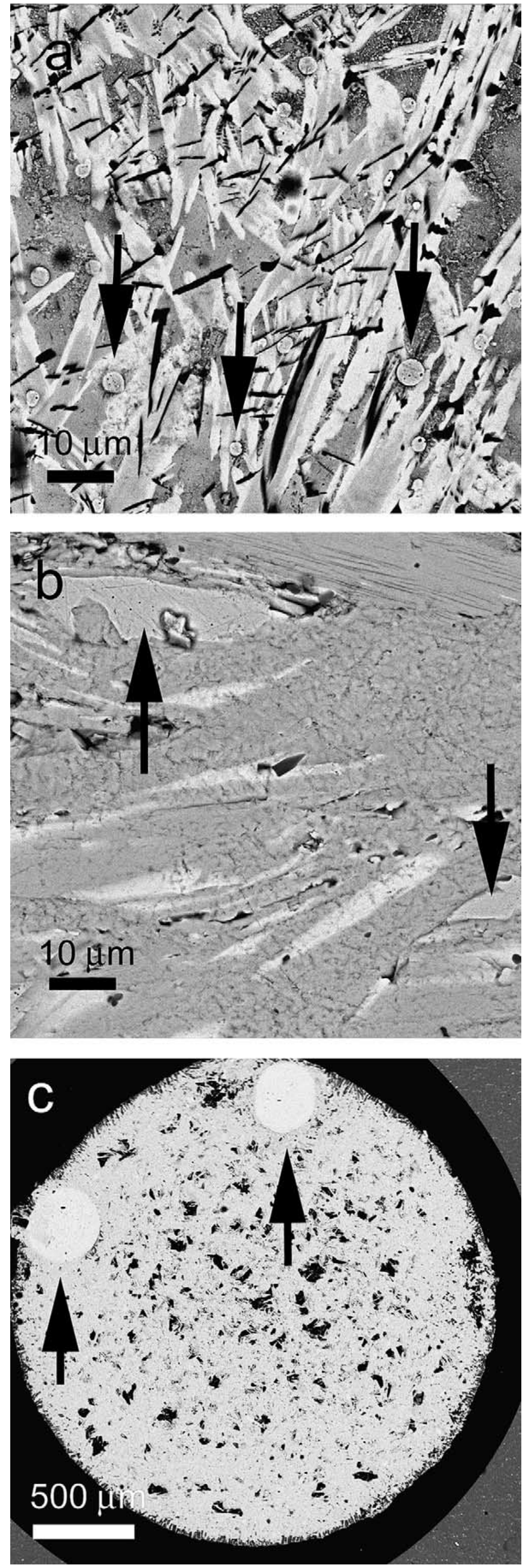

Fig. 1. SEM backscattered electron images of polished samples: (a) as grown longitudinal section; (b) annealed Bi-2212 + 3 wt.% Ag longitudinal section; and (c) annealed Bi-2212 + 10 wt.% Ag transversal section. Ag inclusions are marked with arrows.

particles fill the holes between these superconducting grains (Fig. 1b). This shape change in Ag is due to the formation of a liquid phase[12] and its migration to the elongated holes between superconducting grains, originated in the formation process of Bi-2212 from Bi-2201 and other secondary phases. The number and size of these silver inclusions increases with the silver content. In the case of the higher silver contents (>5%) big spherical particles are formed (Fig. 1c).

To study the mechanical behaviour, flexural strength essays were made on annealed samples. As can be seen on Fig. 2, a very important improvement of mechanical strength is obtained for samples containing 1 wt.% Ag, from values of 115 to 160 MPa. For higher silver contents, the mechanical strength decreases, but it is still higher than for pure Bi-2212 for Ag contents lower than 5 wt.%. This improvement can be related to the new silver shape obtained after annealing, which fills the intergranular holes that appear in the superconducting matrix. Silver between superconducting platelets provide a plastic-flow region and may resist crack propagation by deflecting the crack.[10] The observed decrease on the mechanical properties for Ag contents >5 wt.% is due to the formation of very big spherical silver grains that act as amplifier stress (see Fig. 3b). The changes are not associated with quenching effects due to the thermal treatment because these changes in the flexure strength values are much higher than the values observed in this material using different post-annealing cooling rates,[13] where maximum variations of about a 10% were found.

Fig. 4a shows the temperature dependence of the resistivity as a function of Ag content, it can be seen that T_c is nearly the same for all the samples indicating that Ag do not enter in the superconducting phase. The evolution of the *I–V* characteristics is shown on Fig. 4b. Samples with 3 wt.% Ag exhibit the best transport current values. For higher Ag contents, I_c decreases. This result demonstrates that big Ag grains modify the electrical connectivity among superconducting grains because the big Ag inclusions deteriorate the texture of the adjacent superconducting grains[9] reducing the transport properties.

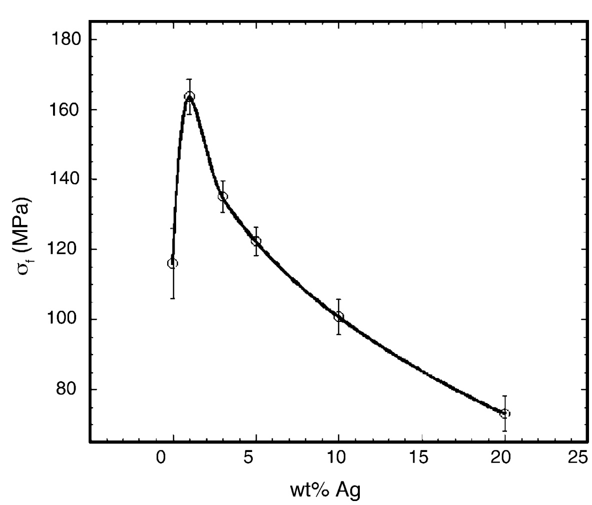

Fig. 2. Annealed rods mechanical performance (three point flexure strength) as function of Ag content.

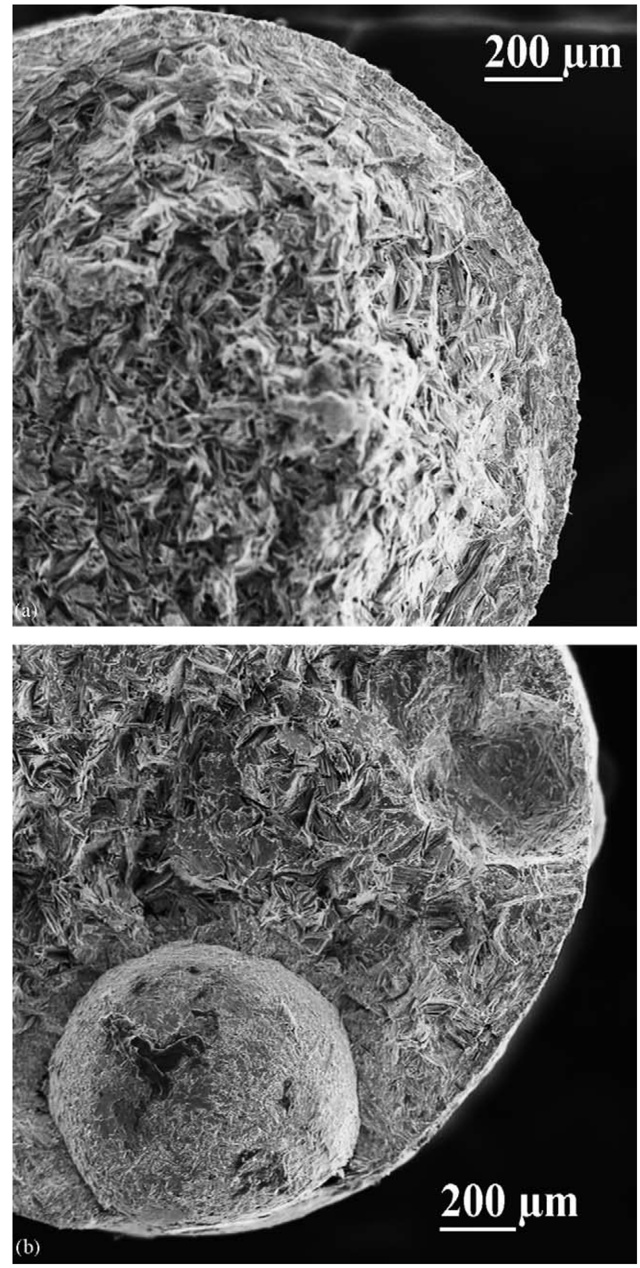

Fig. 3. Fracture micrograph of annealed Bi-2212 + 1 wt.% Ag (a) and 20 wt.% Ag (b) samples tested in three point bending.

The optimal silver content determined in this work is very low when compared with other published works,[9,10] where the mechanical Ag benefits are explained in terms of the ability to reduce the porosity of the samples. The material that is presented in this paper reaches densities higher than 90% of the theoretical one. This explains that the optimal silver content is very low in comparison with other texturing techniques.[9,10]

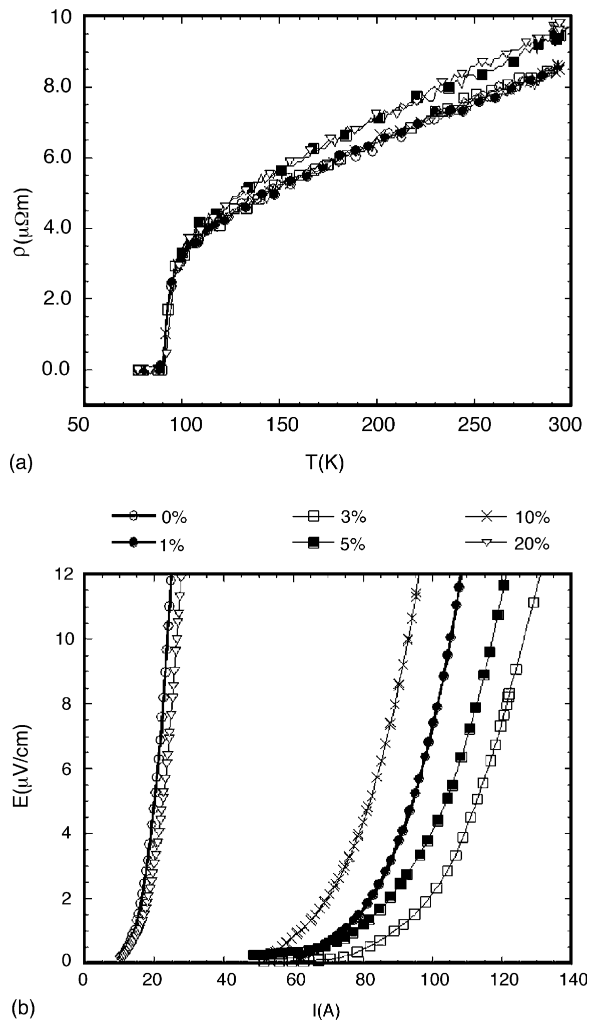

Fig. 4. Electrical characteristics of annealed rods as function of Ag content: (a) temperature dependence of electrical resistivity (1 mA, dc current), and (b) *I–V* curves at 77 K.

4. Conclusions

Bi-2212 textured samples doped with Ag were grown from the melt, through a LFZ process. On as-grown textured rods, Ag appears as spherical particles that change their shape to more elongated polygonal ones after annealing filling holes between superconducting grains. It has been demonstrated that in these dense superconducting materials Ag addition is useful for the improvement of properties when Ag is added in small amounts. For Ag contents higher than 5 wt.% Ag inclusions act as defects, concentrating the stress and weakening the grains connectivity.

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