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Stress corrosion cracking of Bi-2212 thin rods

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Abstract

The flexure strength of $Bi_2Sr_2CaCu_2O_{8+\delta}$ thin rods textured by a laser heated floating zone was measured as a function of the environment (air versus water) at room temperature. Loading rates spanning three orders of magnitude (1, 10 and 100 μm/min) were used to explore their susceptibility to the environmental conditions. These mechanical test were completed with electrical characterization (critical current at 77 K and resistivity from 77 to 300 K) of samples submerged in distilled water for different times (0, 12 and 127 h). While $Bi_2Sr_2CaCu_2O_{8+\delta}$ has been shown, in previous works, to be unstable during contact with water molecules, the textured rods tested in this work are very inert to the water environment, in mechanical and electrical properties, due to the presence of a very thin (∼100 μm) low textured outer ring formed in the grown process.

Keywords: Corrosion; Mechanical properties; Electrical properties; Oxide superconductors; Laser floating zone

1. Introduction

The development of practical applications of high temperature superconductors requires not only the knowledge of their electrical properties, but their mechanical behaviour under different environments. Bulk Bi-2212 superconductors have demonstrated that they are suitable for many applications when they are properly processed,[1] for example, through the laser floating zone technique.[2,3] The Bi-2212 bulk materials textured by this or other techniques[4] have very interesting electrical properties that allow developing fault current limiters and current leads.[5] One of the main advantages of this method is that samples can be rapidly grown due to the large thermal gradients present at the solid–liquid interface.[6] On the other hand, for any practical application, it is necessary to take into account their reactivity to moisture,[7,8] which leads to their chemical degradation and, as a consequence, its effect on their electrical and mechanical properties.

In this work, the environmental susceptibility of Bi-2212 thin rods grown by a laser floating zone method has been measured by means of three-point bending test in air and water, at room temperature. The evolution of the electrical properties, critical current and resistivity, as a function of the immersion time in water are also reported.

2. Experimental

$Bi_2Sr_2CaCu_2O_{8+\delta}$ has been prepared from commercial Bi_2O_3 (Panreac, >98%), $SrCO_3$ (Panreac, >98%), $CaCO_3$ (Panreac, >98.5%) and CuO (Panreac, >97%). They were weighted in the adequate atomic proportions, mixed in an agate ball mill and thermally treated twice under air (12 h at 750 °C and 12 h at 800 °C), in order to decompose carbonates. Cylindrical precursors were manufactured by cold isostatic pressing (200 MPa), and textured rods of approximately 1.70 mm in diameter were grown downwards at 40 mm/h from the precursors through the laser floating zone method, as described elsewhere,[6] using a continuous power Nd:YAG laser beam ($\lambda = 1064$ nm). This processing procedure leads to rods with a highly oriented microstructure, with the *ab* planes parallel to the rod axis.[2] After texturing, in order to obtain the appropriate phase composition (Bi-2212) the rods were subjected to a two step annealing process[9] in air, 50 h at 860 °C followed by 12 h at 800 °C and finally quenched in air to room temperature.

The flexure strength of the rods was measured by three-point bend tests using a fixture of 15 mm loading span in a mechanical testing machine (Instron 5565). The tests were performed in air under stroke control at cross-head speeds of 1, 10 and 100 μm/min at room temperature, with and without (only atmospheric moisture) water. The rods tested in water conditions were immersed in distilled water during 1 h. A drop of water, added with a syringe, covered the central section of the rods during the mechanical test to ensure that the fracture region was immersed

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Table 1
Measured mechanical properties

Environment	Loading rate (μm/min)	σ_f (MPa)	E (GPa)	Weibull parameters	
				σ_o	m
Air	1	133 ± 6	77 ± 3	101	2.8
Air	10	128 ± 4	76 ± 2	107	4.1
Air	100	128 ± 6	73 ± 3	136	7.5
Water	1	127 ± 4	76 ± 2	133	11.1
Water	10	135 ± 5	75 ± 1	141	10.9
Water	100	142 ± 3	77 ± 3	146	16.8

in water during the test. The flexure strength was computed from the maximum load in the test, according to the strength of materials theory for an elastic beam of circular section. For each condition 10 samples were tested. The fracture surfaces of the broken specimens were examined in an scanning electron microscope (JEOL JSM 6400).

Low resistance silver contacts were painted on the samples for electrical characterization. The measurements of the critical current at 77 K, I_c (77 K), and the dependence of the dc resistivity with temperature, $\rho(T)$, were performed on 3 cm long samples using the common four-probe configuration. The current was kept fixed at 1 mA in the resistivity measurements, while the critical currents were determined in self-field using the 1 μV/cm criterion. All the electrical measurements were performed on samples immersed up to 127 h, with intermediate measurements at 0 and 12 h.

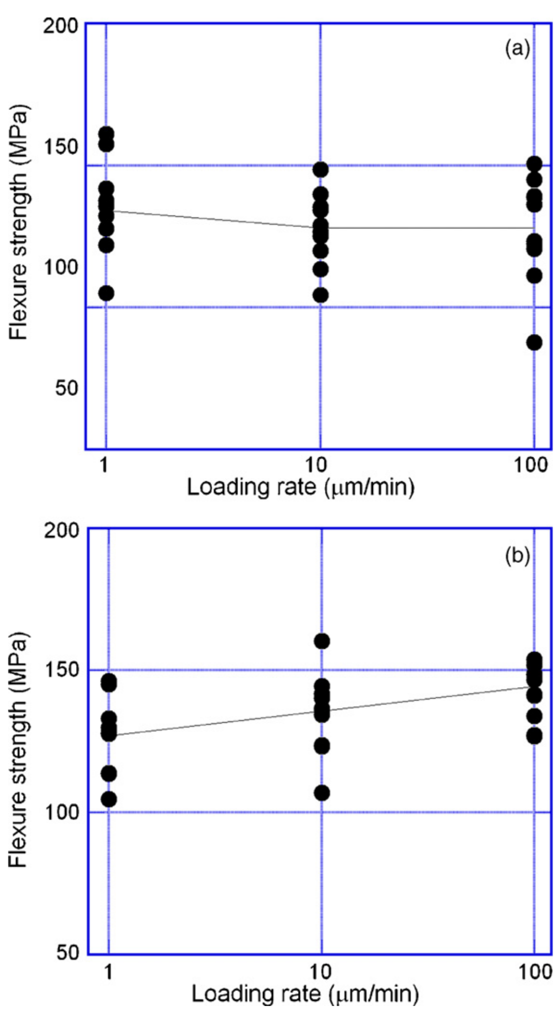

Fig. 1. Flexure strength of Bi-2212 as a function of the loading rate: (a) in air and (b) in water. The displayed lines are passing through the mean values for each condition.

3. Results and discussion

The experimental data determined from the flexure tests at different loading rates can be observed in Table 1, where the average values of the flexural elastic modulus, E, and the flexure strength fracture, σ_f, are displayed, together with their corresponding standard errors. The brittle nature of these ceramics, together with the high anisotropy of their microstructure is reflected in the Weibull parameters found in the bending experiments. The first interesting result in this table is that the fracture strength values are very similar for all the environment conditions and loading rates. When looking the samples measured under air (Fig. 1(a)) the dependence of the fracture strength with the loading rate is not so marked, indicating that the environmental susceptibility of these textured rods to the air moisture is low, as it was previously reported.[10] On the contrary, a small but significant dependence with the loading rates can be observed when samples are tested in water (Fig. 1(b)). This change can be related to the chemical degradation with water,[7,8] which is in agreement with an stress corrosion cracking as a process for the interpretation of the mechanical behaviour of this material. The reaction involved in this degradation mechanism, takes place in a two step process[7,8]:

$$Bi_2Sr_2CaCuO_{8+\delta} + 3H_2O \rightarrow 2Sr(OH)_2 + Ca(OH)_2 + CuBi_2O_4 + CuO \quad (1)$$

$$Sr(OH)_2, Ca(OH)_2 + CO_2 \rightarrow H_2O + SrCO_3, CaCO_3 \quad (2)$$

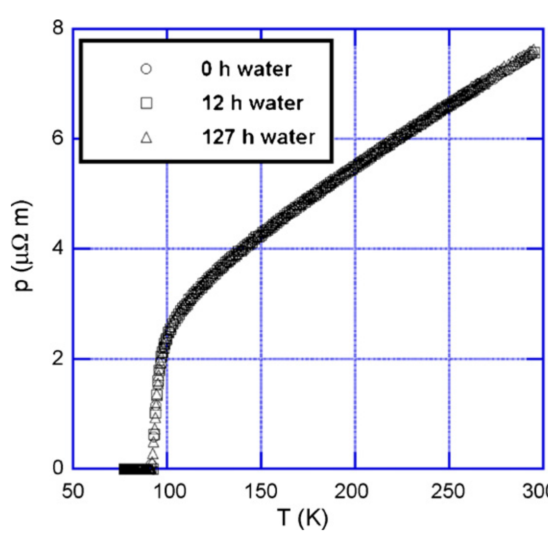

Fig. 2. Electrical resistivity of samples as a function of the immersion time in water.

The subcritical crack growth is a limitation to fracture strength in ceramics. The stable growth of cracks under applied stresses less than that for fast fracture (slow crack growth, SCG) is usually studied by means of the power-law function[11]:

$$v = AK_{\mathrm{I}}^{n} \tag{3}$$

where K_{I} is the stress intensity factor at the tip of the crack and A and n are parameters depending on the material and the environment. The n value can be computed from the slope of the $\log \sigma_{\mathrm{f}}$ versus $\log(\mathrm{d}\varepsilon/\mathrm{d}t)$. The n value obtained in this work for water tested samples is around 42, which is comparable with Al_2O_3 at room temperature in water environment, as it has been reported.[12] This result is unexpected when compared with previous works on the influence of moisture in Bi-2212 bulk samples.[7,8] The water influence is so low that no marked differences in the fractured surfaces have been detected between air and water environment conditions.

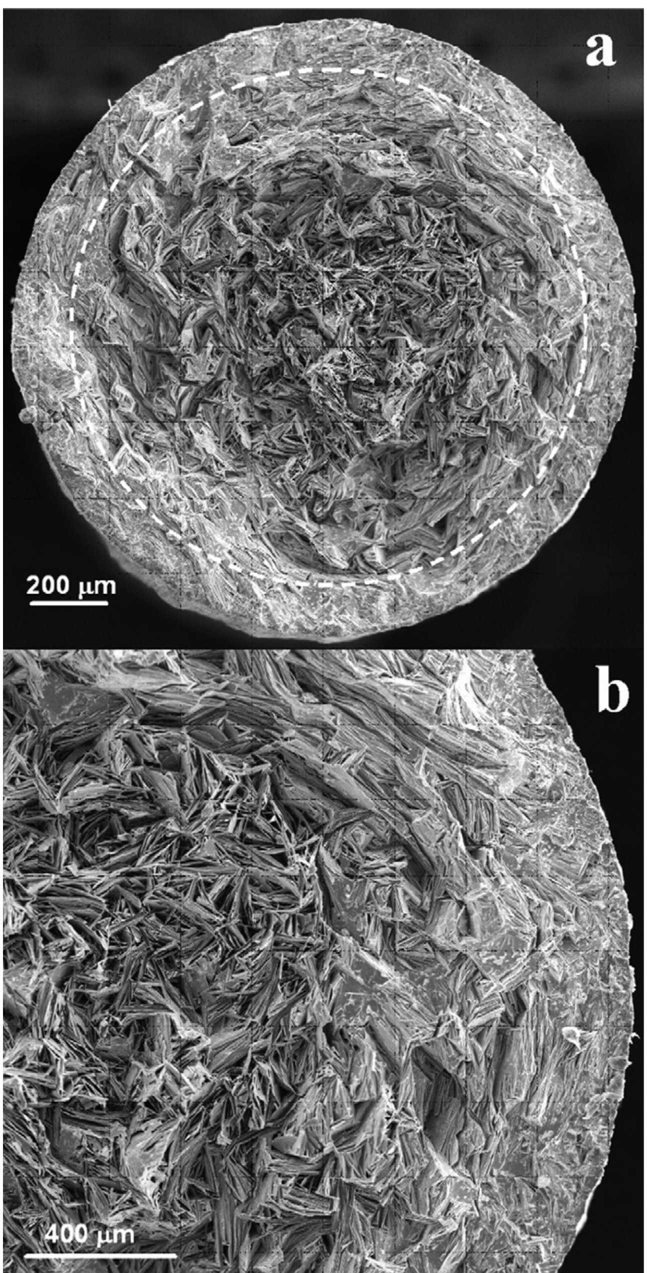

Fig. 3. Typical fracture surface of a Bi-2212 laser heated floating zone textured rod. (a) General view. (b) Detail of the inner (high texture) and outer region (low texture).

As it can be seen in Fig. 2, the electrical resistivity of the samples remains constant, independently of the water exposition time. This is a surprising result, and in our knowledge, never has been reported for this type of materials. Moreover, the critical current has also been measured, and no significant changes have been detected, obtaining values of about 60 A at 77 K in self-field, corresponding to a value of $J_c = 2650\ \mathrm{A/cm^2}$. This effect is related with the special microstructure developed in this material when processed by a LFZ, where a thin outer ring, with a low texture is developed. This ring can be clearly seen in Fig. 3. As it has been previously reported,[10] this zone acts as a protecting layer for the condensed water in the thermal cycling between liquid nitrogen and room temperature. In this work, it is shown that this zone protects not only against condensed water but also in more severe conditions as liquid water immersion. This ring really acts like a sealant preventing chemical degradation reactions with moisture, and even in the liquid water conditions, help to maintain the mechanical and electrical characteristics.

4. Conclusions

The environmental susceptibility of Bi-2212 thin rods textured by a laser heated floating zone was studied by means of three-point bending test in air and in water at room temperature. No significant differences have been found for the strength when the flexure tests were performed in air at three different loading rates. Nevertheless, it was found that the strength of the rods tested in water slightly depends on the loading rate, with a n value of 42. The low reactivity of these rods with water has been contrasted with the evolution of the electrical properties. When comparing critical current at 77 K and electrical resistivity between 77 and 300 K, no differences were found for samples submerged in water for 0, 12 and 127 h.

While $Bi_2Sr_2CaCu_2O_{8+\delta}$ has been shown, in previous works, to be unstable during contact with water molecules, the thin textured rods tested in this work, show to be very inert to the environment, with respect to the mechanical and electrical properties, due to the presence of a thin (∼100 μm) low textured outer ring formed in the growth process. The self-coating protection developed in this laser heated floating processes has demonstrated its performance, both in air and in water environment, as it has been reflected in both, mechanical and electrical properties.

Acknowledgements

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