Dynamic fatigue behaviour of Ag-doped Bi-2212 textured thin rods

M A Madre1, Sh Rasekh, J C Diez and A Sotelo
ICMA (UZ-CSIC), Depto. de Ciencia y Tecnología de Materiales y Fluidos, C/María de Luna 3, E-50018, Zaragoza (Spain)

E-mail: amadre@unizar.es

Abstract. The flexural strength of 1 wt.% Ag-doped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ thin rods textured by a laser heated floating zone was measured as a function of the environmental conditions (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 tests were completed with electrical characterization (critical current at 77K and resistivity from 77 to 300 K) of samples submerged in distilled water for different times (0, 12 and 120h). While Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ has been shown, in previous works, to be unstable during contact with water molecules, the Ag-doped Bi-2212 textured rods tested in this work are very inert to the water environment, with respect to their mechanical and electrical properties, due to the presence of a narrow (≈150 µm) low textured outer ring formed in the growth process.

1. Introduction
The development of practical applications of bulk high temperature superconductors requires not only the knowledge of their electrical properties, but their mechanical behavior 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]. A second additional advantage is the absence of crucible, avoiding external contamination of textured samples during their processing.

However, the poor mechanical characteristics of this kind of materials [7], due to their ceramic nature, impose limitations for practical applications. Some attempts to improve their mechanical properties have been performed by means of Ag additions on BSCCO compounds [8-10].

On the other hand, for any practical application, it is necessary to take into account their reactivity to moisture [11, 12], 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 Ag-doped 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 electrical resistivity, as a function of the immersion time in water, is also reported.
2. Experimental

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} + 1 \text{ wt.}\% \text{Ag}$ materials have been prepared from commercial $\text{Bi}_2\text{O}_3$ (Panreac, 98+%), $\text{PbO}$ (Panreac, 99+%), $\text{SrCO}_3$ (Panreac, 98+%), $\text{CaCO}_3$ (Panreac, 98.5+%), $\text{CuO}$ (Panreac, 97+) and Ag (Aldrich, 99.9+) powders. They were weighed in the adequate atomic proportions, and, among the many different synthetic methods [13], the sol-gel method via nitrates has been selected due to the good solubility of $\text{AgNO}_3$, as well as the whole metallic nitrates, in dilute nitric acid. Appropriate proportions of citric acid and ethilenglycol were also added to the nitrates solution, followed by heating on a hot plate at 50-80 ºC in order to form the gel by polymerization between citric acid and ethilenglycol when the pH is reduced by decomposition of the metallic nitrates and the $\text{HNO}_3$ added in excess, following the reactions (1) and (2), corresponding to an esterification process (equation 1) and to the polymerisation one (equation 2):

\[
\text{R-C-OH} + \text{HO-R'-OH} \rightarrow \text{H}_2\text{O} + \text{R-C-O-R'-OH} \quad (1)
\]

\[
\eta \left( \text{H}_2\text{O-R-C-R'-OH} \right) \rightarrow \eta \left( \text{R}_{\text{a}}\text{O-R}_{\text{a}}\text{O} \right) + \eta \text{H}_2\text{O} \quad (2)
\]

Further heating leads to the evaporation of the solvent and, finally, to a self combustion of the solid gel. The so obtained powders were thermally treated twice at 750 and 800 ºC for 6 hours, with an intermediate grinding, to avoid grain growth and assure total carbonates decomposition, which is a critical step in order to avoid bubbles formation in the melting process, disturbing the solidification front.

These prereacted powders were then used to prepare cylindrical precursors, 120 mm long and 2-3 mm diameter, approximately, by cold isostatic pressing with an applied pressure of 200 MPa during 1 minute. The obtained cylinders were used as feed in a directional solidification process performed in a laser floating zone melting (LFZ) installation described elsewhere [6]. The textured bars were obtained using a continuous power Nd:YAG laser ($\lambda = 1064$ nm), under air, at a growth rate of 30 mm/h and a relative rotation of 18 rpm between the seed and feed. Using these growth conditions and adjusting the laser power input to obtain a molten zone of approximately 1-1.5 times the rod diameter, it is possible to obtain stable growth, which allows the fabrication of very homogeneous bars.

All the studied materials present an incongruent melting and, in consequence, after texturing, it is necessary to perform a thermal treatment in order to form the Bi-2212 superconducting phase [14]. This annealing process is performed under air, and consisted in two steps: 60 h at 850ºC, followed by 12 h at 800ºC and, finally, quenched in air to room temperature.

| Environment | Loading rate ($\mu$m/min) | $\sigma_t$ (MPa) | Weibull parameter, $m$ |
|-------------|-------------------------|----------------|-----------------------|
| Air         | 1                       | 160 ± 7        | 8.1                   |
| Air         | 10                      | 164 ± 5        | 11.8                  |
| Air         | 100                     | 169 ± 5        | 11.5                  |
| Water       | 1                       | 166 ± 6        | 11.1                  |
| Water       | 10                      | 174 ± 5        | 14.2                  |
| Water       | 100                     | 183 ± 4        | 16.8                  |

The flexural strength of the rods was measured by three-point bend tests using a fixture of 10 mm loading spam 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 $\mu$m/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 before the test. A drop of water, added with a syringe, covered the central section of
the rods during the mechanical tests to ensure that the fracture region was immersed in water during the whole test. The flexural strength was computed from the maximum load achieved 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 a scanning electron microscope (JEOL JSM 6400).

Low resistance silver contacts were painted on the samples for electrical characterization, before the annealing process. 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 30 mm long samples using the common four-probe configuration. The current was kept fixed at 1mA in the resistivity measurements, while the critical currents were determined in self-field using the standard 1 \( \mu \)V/cm criterion. All the electrical measurements were performed on samples immersed in water up to 120 h, with intermediate measurements at 0 and 12 h.

3. Results and discussion

The experimental data determined from the flexure tests at different loading rates are displayed in table 1, where the average values of the flexural strength fracture, \( \sigma_f \), are displayed, together with their corresponding standard errors. The brittle nature of these ceramic materials, together with the high anisotropy of their microstructure is reflected in the Weibull parameter, \( m \), calculated from the data obtained in the bending experiments. An interesting result shown in this table is that the fracture strength values are not so different for each of the environmental conditions and loading rates (from 160 MPa at 1 \( \mu \)m/min under air to 183 MPa at 100\( \mu \)m/min under water). When looking the samples measured under air, the dependence of the mean fracture strength with the loading rate is not so marked (\( \Delta \approx 5\% \), from 160 to 169 MPa), indicating that the environmental susceptibility of these textured rods to the moisture is low. On the contrary, a small but more significant dependence with the loading rates can be observed when samples are tested in water (\( \Delta \approx 10\% \), from 166 to 183 MPa).

![Figure 1](image)

**Figure 1.** Flexural strength of Ag-doped Bi-2212 materials as a function of the loading rate, measured a) in air; and b) in water. The displayed lines are passing through the mean values for each loading rate.

In order to show this evolution, the individual strength results for each sample and conditions, are displayed in figure 1 (figure 1a for measurements in air and figure 1b, in water). Also, a line is plotted passing through the mean values for each testing speed in order to clarify the strength dependence with the punch displacement speed. This change can be related to the chemical degradation with water [11, 12], which is in agreement with a stress corrosion cracking as a process for the interpretation of the mechanical behavior of this material. The reaction involved in this degradation mechanism takes place in two subsequent step processes, described by the chemical reactions:
\[
\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8 + 3\text{H}_2\text{O} \rightarrow 2\text{Sr(OH)}_2 + \text{Ca(OH)}_2 + \text{CuBi}_2\text{O}_4 + \text{CuO} \quad (3)
\]

\[
\text{Sr(OH)}_2, \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{SrCO}_3, \text{CaCO}_3 \quad (4)
\]

The slightly higher mean values for samples measured in water, than those measured in air, can be explained by the formation of a continuous water layer inside the cracks, which avoids the surface contact with the CO\(_2\) necessary to perform the reaction described in equation (4).

The subcritical crack growth is a limitation to fracture strength in ceramics. The stable growth of cracks under applied stresses lower than those for fast fracture (slow crack growth, SCG) is usually studied by means of the power-law function [15]:

\[
v = AK_1^n
\]

where \(K_1\) 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 \(\lg \sigma_t\) versus \(\lg (\text{d}e/\text{d}t)\). The \(n\) value obtained in this work for water tested samples is around 47, which is the same order as Al\(_2\)O\(_3\) at room temperature in water environment, as it has been previously reported [16]. This result is unexpected when compared with previous works on the influence of moisture in Bi-2212 bulk samples [11, 12]. The water influence is so low that no marked differences in the fractured surfaces have been detected between air and water environment conditions. On the other hand, when samples are measured in air, the \(n\) value is increased spectacularly to 82, which is in the order of \(\alpha\)-SiC measured at high temperatures [16].

![Figure 2. Electrical resistivity of samples as a function of the immersion time in water](image)

As it can be seen in figure 2, the electrical resistivity of the samples remains constant, independently of the water exposition time. This seems to be a surprising result when taking into account the high reactivity of this Bi-2212 compounds with moisture, but it is in agreement with the results obtained in previous works for the pure Bi-2212, when it is processed using the LFZ texturing technique [17]. Moreover, the critical currents have also been measured, and no significant changes have been detected, obtaining values of about 75A at 77K in self-field, corresponding to a value of \(J_c = 3570\) A/cm\(^2\). This good behavior against moisture is related with the special microstructure developed in this material when processed by a LFZ, where a thin outer ring, with low texture and slightly lower grain size than in the inner part, is developed. This ring can be clearly seen in figure 3. As it has been previously reported [17] this zone is acting as a protecting layer against liquid water immersion. This ring really acts like a sealant preventing chemical degradation reactions with
moisture, and even in the liquid water conditions, helping to maintain the mechanical and electrical characteristics.

![Figure 3. Typical fracture surface of an Ag-doped Bi-2212 textured rod. (a) General view, (b) detail of the outer ring (low texture), and the inner zone (high texture)](image)

4. Conclusions
The environmental susceptibility of 1wt.% Ag-doped 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 an $n$ value of 47, while for air tested samples is around 82. The low reactivity of these rods with water has been contrasted with the evolution of the electrical properties. When comparing critical current values at 77K and electrical resistivity curves between 77 and 300 K, no differences were found for samples submerged in water for 0, 12 and 120 h.

While $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8^{+\delta}$ has been shown, in previous works, to be unstable during contact with water molecules, the thin Ag-doped Bi-2212 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 ($\approx$150 µm) low textured outer ring formed in the growth process. The self-coating protection developed in this laser growth process has demonstrated its performance, both in air and in water environment, as it has been reflected in both, mechanical and electrical properties.

Acknowledgments
The authors are indebted the Spanish Ministry for Education and Science (MAT 2005-06279-C03-01) and to the Aragón Regional Government (Research Groups T74 and T12) for financial support. The technical support from C. Gallego, C. Estepa and J. A. Gómez is also acknowledged.

References
[1] Chen M, Donzel L, Lakner M and Paul W 2004 *J. Eur. Ceram. Soc.* 24 1815-22
[2] Garnier V, Caillard R, Sotelo A and Desgardin G 1999 *Physica C* 319 197-208
[3] Costa F M, Silva R F and Vieira J M 2001 *Supercond. Sci. Technol.* 14 910-20
[4] Diez J C, Angurel L A, Miao H, Fernández J M and de la Fuente G F 1998 *Supercond. Sci. Technol.* 11 101-6
[5] Ester F J and Peña J I 2007 *Bol. Soc. Esp. Ceram.* V. 46 240-46
[6] Angurel L A, Diez J C, Martinez E, Peña J I, de la Fuente G F and Navarro R 1998 Physica C 302 39-50
[7] Pastor J Y, Poza P and Llorca J 1999 J. Am. Ceram. Soc. 82 3139-44
[8] Salazar A, Pastor J Y and Llorca J 2003 Physica C 385 404-14
[9] Joo J, Singh J P, Warzynski T, Grow A and Poeppel R B 1994 Appl. Supercond. 2 401-10
[10] Sotelo A, Mora M, Madre M A, Diez J C, Angurel L A and de la Fuente G F 2005 J. Eur. Ceram. Soc. 25 2947-50
[11] Jin S G, Zhu Z Z, Liu L M and Huang Y L 1990 Solid State Commun. 74 1087-90
[12] Lee D, Kondrate Sr R A and Taylor J A 2001 Physica C 350 1-16
[13] Ruiz M T, de la Fuente G F, Badia A, Blasco J, Castro M, Sotelo A, Larrea A, Lera F, Rillo C and Navarro R 1993 J. Mat. Res. 8 1268-76
[14] Mora M, Martinez E, Diez J C, Angurel L A and de la Fuente G F 2000 J. Mat. Res. 15 614-20
[15] Munz D and Fett T 2001 Ceramics: Mechanical Properties, Failure Behaviour, Materials Selection, Springer
[16] Choi S R, Nemeth N N and Gyekenyesi J P 2005 Fatigue Fract. Eng. 28 489-97
[17] Diez J C, Sotelo A, Mora M, Amaveda H and Madre M A 2007 J. Eur. Ceram. Soc. 27 3963-66