Influence of the heat treatment profiles on the development of highly textured Ag/Bi2212 monofilamentary tapes

A R Bigansolli, E Cursino, F A Santos and D Rodrigues Jr
Superconductivity Group, Department of Materials Engineering, FAENQUIL, Lorena, SP, Brazil 12600-970
E-mail: durval@demar.faenquil.br

Abstract. The use of superconducting ceramics, with higher critical temperatures and higher operation temperatures, leads to economy of cryogenic liquids and systems. One of the largest problems in the practical use of superconducting ceramics is the intrinsic anisotropy of the critical currents. The present work describes a study of the texturing process in Ag/Bi2212 monofilamentary tapes, permitting the optimized choice of the heat treatment profiles to obtain superconducting phases close to the stoichiometric, with high texturing and high critical current densities $J_c$. The samples of Ag/Bi2212 tapes were obtained using the powder-in-tube (PIT) process with partial melting, treated at different maximum temperatures and with fixed cooling rate and isotherm at low temperature under oxygen flow at atmospheric pressure. The microstructural, electrical and superconducting characterization showed that the Ag/Bi2212 tapes submitted to different heat treatment profiles had significant improvements on the texturing and on the superconducting and microstructural characteristics and properties. The tapes treated with the maximum temperature of 890 ºC for only 10 minutes followed by a cooling rate of –5 ºC/h and 5 hours at the 830 ºC isotherm presented best critical current densities of 7.5x10⁴ A/cm², at 4.2 K and 5 T; and 1.4x10⁵ A/cm², at 4.2 K and 0 T. This very short step at high temperature is extremely important for magnet development and applications.

1. Introduction
The applications of high critical temperature ceramic superconductors (HTSC) in power systems is defined, mainly, by their transport critical current densities $J_c$. Superconducting ceramics with high $J_c$ can be used in the winding or current leads of superconducting magnets [1].

The most important obstacle to obtain high $J_c$ in this type of superconductors is the weak links between high-angle grains [2]. The texturing development in these superconductors efficiently decreases the number of high-angle grain boundaries, increasing the values of $J_c$. Besides that, the low density and the presence of residual non-superconducting phases are other obstacles to obtain high $J_c$ in these materials [3,4]. Even with a highly textured microstructure, particles of non-superconducting phases will still decrease $J_c$ in superconducting Bi$_x$Sr$_y$CaCu$_2$O$_{x+8}$ (Bi2212) samples.

The processing at temperatures close to the ceramic melting points (partial melting process) can lead to denser microstructures. However, this procedure induces the formation of non-superconducting phases. The decomposition of the Bi2212 phase occurs at the melting temperature while the non-superconducting phases are stable and tend to grow in the presence of the liquid phase. During the solidification process, these phases react with the liquid forming the Bi2212 phase. If the decomposition is not complete, or if the non-superconducting phases grow faster than the Bi2212 phase, large quantities of residual secondary phase particles will persist in the final material,
decreasing $J_c$ [4,5]. Some techniques are been developed to efficiently overcome these obstacles. For applications, the heat treatment profiles must have specific characteristics to avoid interference on the properties of the structural materials and the resins used in the superconducting magnets. Heat treatments at high temperatures and for long periods of time must be avoided.

The present work shows the results of highly textured Ag/Bi2212 monofilamentary tapes developed using the powder-in-tube (PIT) method. The definition of the heat treatment maximum temperatures and the permanence times at these temperatures, along with fixed cooling rates and low temperature isotherms, can enable the optimization of the heat treatment profiles, opening a large variety of technological applications. The results clearly showed the influence of different profiles on the texturing conditions of Ag/Bi2212 monofilamentary tapes. This information will help the understanding of the mechanisms involved in the fabrication of highly textured Bi2212 ceramic superconductors.

2. Experimental Procedure

The superconducting tapes were prepared using commercial superconducting powder with the stoichiometry close to Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi2212). The powder was treated in air at 200 °C for 1 hour and it was manually compacted in a pure silver tube with an outer diameter of 5 mm and an inner diameter of 3 mm, with one end closed with a 3 mm diameter copper tap. The set was placed in a quartz tube, evacuated and slowly heated up to 700 °C in a vertical furnace. The set was treated at this temperature for 18 hours and it was slowly cooled down to room temperature. This was a procedure to remove water. After this step, the material was removed from the furnace and the other end of the silver tube was closed with another copper tap. The tube was gradually deformed by swaging until the outer diameter of 2.3 mm and by rolling to a thickness around 130 μm.

The samples were heat treated in a tubular furnace under vacuum and pure oxygen atmosphere following the profile showed in Figure 1. The heat treatments consisted of the use of two maximum temperatures of treatment (890 °C and 905 °C), with two different permanence times (10 minutes and 2 hours), with a cooling rate of –5 °C/h from 890 °C to 830 °C and an annealing isotherm at 830°C for 5h. After these steps, the furnace temperature was decreased to room temperature in 1 hour.

After heat treatment, the samples were cooled in liquid nitrogen and fractured to expose the transversal sections for the microstructural characterization using Scanning Electron Microscopy using a LEO1450VP SEM in the backscattered electrons mode. X-ray diffraction (XRD) measurements were obtained on the internal surface of the Bi2212 phase parallel to the tape surface, after cutting and opening the tapes. The samples were characterized with XRD using a Philips X-ray diffractometer with CuKα radiation. The obtained results allowed the evaluation of formation and evolution of phases in textured samples of Ag/Bi2212 superconductors. The superconducting characterization was performed through the measurements of critical temperature $T_c$ and critical current $I_c$.

![Figure 1. Heat treatment profiles used for the Ag/Bi2212 monofilamentary tapes.](image)

3. Results and Discussion
Figures 2 and 3 show the XRD patterns and SEM micrographs, respectively, for the tapes treated with the maximum temperatures at 890 ºC and 905 ºC, with two different permanence times of 10 minutes and 2 hours, and cooling time of 12 hours (cooling rate $T_x = -5$ ºC/h) from the maximum temperature to 830 ºC. In Figure 2, the X-ray characteristic peaks show the presence of only the Bi2212 phase in all samples. One can see very good texturing for the samples treated with the maximum temperature at 890 ºC analyzed through the many $(00l)$ peaks with high intensities, and few peaks with $(hk0)$ orientation. Good texturing can not be observed for the samples treated with the maximum temperature at 905 ºC. Peaks of silver can be observed in all XRD, coming from the Ag tape.

The maximum temperature during heat treatment of Ag/Bi2212 monofilamentary tapes is very important to obtain highly textured samples. One can note important differences on the texturing behavior between the samples treated at both temperatures, while the last one decreased the texturing. The permanence time at the maximum temperature also influences the texturing process.

Figure 3 shows the formation of platelets with morphology varying accordingly to the heat treatment maximum temperature. The best textured sample was obtained for the tape treated with a maximum temperature of 890 ºC and permanence time of 2 hours. Again, it can not be observed good texturing for the tapes treated with the maximum temperature of 905 ºC. The results obtained with SEM characterization agree with the XRD results and describe a texturing evaluation procedure that can be used to analyze the heat treatment profiles. These profiles are defined to optimize the transport properties and phase homogenization aiming the use of the tapes in superconducting application [6].

The transition critical temperature characterization of the treated samples is described in Table 1. The measurements were performed using the four-probe method. The values of $T_c$ were obtained as the middle of the transition, calculated between the 10% and 90% of the transition height. The half-width of the superconductor-normal transition defined $\Delta T_c$. The samples treated at the maximum temperature of 890 ºC presented sharper transitions with onset temperatures around 80 K, describing the behavior of very homogeneous superconducting phases, close to the Bi2212 stoichiometry.

![Figure 2](image2.png)

**Figure 2.** X-Ray diffraction of the heat treated samples with maximum temperature of 890 ºC and permanence times of 10 minutes (a) and 2 h (b), and with maximum temperature of 905 ºC and permanence times of 10 minutes (c) and 2 h (d).

![Figure 3](image3.png)

**Figure 3.** SEM micrographs of the heat treated samples with maximum temperature of 890 ºC and permanence times of 10 minutes (a) and 2 h (b), and with maximum temperature of 905 ºC and permanence times of 10 minutes (c) and 2 h (d).

The measurements of critical currents versus applied magnetic field were performed at 4.2 K, in liquid helium bath, using the four-probe method. It was used a Maglab EXA Oxford system, with maximum magnetic field of 9 T. Figure 4 shows the values of the critical current densities $J_c$, obtained...
dividing the critical current $I_c$ by the area of the superconducting ceramic in the samples obtained using SEM analysis. The experimental data of $J_c$ vs. $H$ shows that the texturing is extremely important for the current transport behavior. In some cases, the measured $J_c$ at a given applied magnetic field was almost 10 times higher, when compared samples treated using different heat treatment profiles.

**Table 1.** Critical temperature and transition half-width $T_c$ of the samples.

| Samples            | $T_c$ (K) | $\Delta T_c$ (K) |
|--------------------|-----------|-------------------|
| 890 ºC/10min/12h/5h| 75.1      | 2.8               |
| 890 ºC/2h/12h/5h   | 79.5      | 1.5               |
| 905 ºC/10min/12h/5h| 76.5      | 2.0               |
| 905 ºC/2h/12h/5h   | 55.3      | 9.6               |

**Figure 4.** Critical current densities versus applied magnetic field measured at 4.2 K for the heat treated samples with maximum temperatures of 890 ºC and 905 ºC.

4. **Conclusion**

All tapes heat treated with the maximum temperature of 890 ºC showed high texturing, with the formation of the platelet-like structures. The results obtained by XRD agree with the results obtained by SEM. The texturing of Ag/Bi2212 tapes depends greatly on the heat treatment profiles. The maximum temperature of melt-texturing is a very important parameter of heat treatment, together with the permanence time at high temperature and the cooling rates, influencing the process of texturing [6]. The results presented in this paper can be directly used to develop highly textured Bi2212 tapes to be used in high temperature - high current magnets and applications.

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**References**

[1] Holesinger T G, et al 1998 *Physica C* 294 161
[2] Chen W P, et al 1999 *J. of Cryst. Growth* 204 69
[3] Salamati H, et al 2004 *Physica C* 403 60
[4] Sager D, et al 2004 *Physica C* 405 103
[5] Zhu W, et al 2001 *IEEE Trans. Appl. Supercond.* 11 3030
[6] Rodrigues Jr D, et al 2005 *IEEE Trans. Appl. Supercond.* 15(2) 2546