Successful production of Solution Blow Spun YBCO+Ag complex ceramics
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Highlights

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- synthesis of precursor solution with YBCO+Ag applicable to solution blow spinning
- production of fabric-like ceramic from sol-gel route
- shrinkage of samples due to Ag-addition
Successful production of Solution Blow Spun YBCO+Ag complex ceramics

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ABSTRACT

YBCO fabrics composed of nanowires, produced by solution blow spinning (SBS) are so brittle that the Lorentz force produced by induced currents can be strong enough to damage them. On the other hand, it is known that silver addition improves the mechanical and flux pinning properties of ceramic superconductors. Thus, in this work, we show how we successfully obtained a polymeric precursor solution containing YBCO+Ag salts, which can be spun by the SBS route to produce ceramic samples. Yttrium, barium, copper, and silver metal acetates, and polyvinylpyrrolidone (PVP) (in a ratio of 5:1wt [PVP:acetates]) were dissolved in a solution with 61.5 wt% of methanol, 12 wt% of propionic acid, and 26.5 wt% of ammonium hydroxide, together with 6 wt% of PVP in solution. Three different amounts of silver (10 wt%, 20 wt%, and 30 wt%) were used in YBa2Cu3Ox−y. The TGA characterizations revealed a lowering of crystallization and partial melting temperatures by about 30 °C. SEM images show that after burning out the polymer, a fabric composed of nanowires of diameters up to 380 nm is produced. However, after the sintering process at 925 °C for 1 h, the nanowires shrink into a porous-like sample.

1. Introduction

The main applications of superconductors are based on devices made by low-temperature materials like NbTi [1] and Nb3Sn [2]. However, since the discovery of ceramic high-temperature superconductors (HTS), efforts have been made to develop materials and devices with properties and forms specific to each required application. The pros of using HTS in turbines, generators, motors, magnetic shielding, and NMR/MRI are the reduced weight, high efficiency, compact size, low noise, high trapped fields, and so on [3, 4]. On the other hand, the cons of using HTS are their high production cost, high ac-losses, non-homogeneous trapped field distribution, and high cost and reliability of the cooling systems. Some of these issues, however, can be solved by producing materials following facile and low-cost routes and aiming for high values of critical current density $J_c$ and its homogeneous distribution along the length of the materials. Additionally, high porous superconductors, such as those produced by solution-blown spinning (SBS) [5, 6], electrospinning [7, 8], and in foam-like structures [9, 10], could be used to increase cooling efficiency due to their increased surface areas.

Particularly in the case of SBS, the samples have a fabric-like structure formed by network of wires that produces a thin porous material. However, as can be seen by the data in Ref. [11] the samples are very fragile; they are pulverized during magnetic measurements by the Lorentz force generated by the induced currents in the wires. Therefore, to study their superconducting properties in a wide range of fields and temperatures, it is necessary to improve their mechanical properties.

Research works carried out on bulk (RE)BCO materials, specially in YBa2Cu3O7−x (YBCO) system, showed that both the the mechanical [12, 13, 14, 15] and superconducting [15, 16, 17] properties could be significantly improved through addition of silver. Some of the other benefits of adding silver is that it does not chemically react with YBCO [17, 18, 19], it improves pinning sites [20], it modifies weak-links [21, 22, 23], and it enhances $J_c$ [18, 24].

A variety of silver composites have been added in YBCO system, such as metallic Ag [18], Ag2O [12], and AgNO3 [13, 24]. The samples were usually produced by solid-state reaction [13, 18, 24], melting-growth-like processes [12], and by electrochemical routes [25]. In Ref. [26], a sol-gel chemical route was used to dope the barium site by silver in the production of YBCO pellets. It is reported that high concentrations of silver depreciate the superconducting properties but in small concentrations, it slightly enhances the critical temperature $T_c$ and critical current density $J_c$. However, as discussed in Ref. [27], there is some controversy as to the extent to which Ag can be doped into YBCO samples. Also, to our best knowledge, there is no information about how the inclusion of silver affects the production process of porous samples using chemical routes, such as in SBS.

The SBS technique was first reported in Ref. [28]. In such a technique, polymer solutions are spun by compressed air from an inner needle up to a collector [28, 29]. Along the working distance i.e. the space between the needle and the collector, the solvents have to evaporate, allowing the for-
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Table 1
List of reagents used in the synthesis of precursor solutions.

| Reagents               | Chemical formula | Purity (%) | Brand            |
|------------------------|------------------|------------|------------------|
| Yttrium acetate        | C₆H₉O₆·H₂O       | 99.9       | Sigma            |
| Barium acetate         | C₆H₇BaO₄         | 99         | Sigma-Aldrich    |
| Copper acetate         | C₆H₇CuO₂H₂O      | 99         | Sigma-Aldrich    |
| Silver acetate         | C₆H₇AgO₂         | 99         | Sigma-Aldrich    |
| Poly(vinylpyrrolidone)*| (C₆H₉NO)n        | 99.99      | Sigma-Aldrich    |
| Propionic acid         | C₆H₈O₂           | 99.5       | Sigma-Aldrich    |
| Methanol               | CH₃OH            | 99.8       | Vetec            |
| Ammonium hydroxide     | NH₄OH            | PA         | Dinamica         |

*PVP = 1.300.000 g mol⁻¹

Table 2

2. Materials and Methods

One-pot-like method [30] was used to synthesize the precursor solution, and the reagents used are shown in Table 1. All salts are heated at 100 °C for about 24 h before being weighed, ensuring that there is no moisture in the salts. This is particularly important as some of these salts are hydrophilic in nature.

2.2. Solution-blow spinning

A 10 ml syringe was connected to a 25G (diameter of 0.5 mm) needle. The air pressure of the compressed air cylinder was adjusted to 1 kPa and the working distance between the needle and the collector was set to 40 cm. The cylindrical collector was rotated at 40 rpm and the solution within the syringe was injected into the compressed gas airflow at a rate of 3 ml h⁻¹. A halogen light was placed above the working distance to locally heat the ejected polymer jet, evaporating the solvents prior to the jet’s impact onto the rotating collector.

2.3. Heat-treatments

The as-collected sample was firstly heat-treated at 100 °C for 1 h and then at 150 °C for another 1 h with a heating rate of 5 °C min⁻¹. Some portions of that sample were then used to obtain SEM images. The polymer decomposition was carried out at 600 °C for 3 h ramping the temperature up and down at a rate of 1 °C min⁻¹. Some pieces of the sample at that stage were also used to make SEM analysis. The synthesis was carried out in a tube furnace. The heat-treatment consisted of increasing the temperature from room temperature to 820 °C at 3 °C min⁻¹ and dwelling for 14 h. During the heating process, flowing O₂ was turned on at 500 °C. After that dwell period, the temperature was increased at

Figure 1: (a) The YAg10 precursor solution. (b) Precursor solution loaded in a 10 ml syringe used in the SBS technique.
1 °C min⁻¹ to 925 °C and this was held for 1 h. Then, also at 1 °C min⁻¹, the temperature was decreased to 725 °C for 6 h; then at 3 °C min⁻¹ to 450 °C for 24 h. Finally, the O₂ gas flow was turned off and the temperature was decreased to room temperature at 3 °C min⁻¹.

2.4. Characterizations

Thermogravimetric measurements were carried out on the samples YAg0 and YAg10 (obtained after a heat-treatment at 600 °C), employing TA Instrument, model SDT-Q600. Measurements were carried out under flowing compressed air at a rate of 100 ml min⁻¹ and the temperature was increased from 25 °C to 1000 °C at a rate of 10 °C min⁻¹. For the scanning electron microscopy (SEM) measurements, an EVO LS15 Zeiss operated at 20 kV was used. For that, the samples were attached in an aluminum sample holder with carbon tape, and gold was sputtered on their surface for 2 min (5 nm average thickness) using a QUORUM Model Q150T E. The diameter distribution was measured using a randomly selected set of 100 wires and the free software package ImageJ. The x-ray analysis (XRD) was performed in a Shimadzu XDR-6000 diffractometer with CuKα radiation (wavelength: 1.5418 Å). The displacement ranged from 2θ = 5° to 60° at a scan rate of 1 °C min⁻¹ and measuring in steps of 0.02°.

3. Results and Discussions

Thermal analysis was carried out on two samples YAg0 and YAg10, after both were heat treated at 650 °C. About 15 mg of each sample was used for the measurement and the data obtained is shown in Figure 2. Both the samples exhibited a similar weight loss, as can be seen from the curves in Figure 2. The mass lost between 25 °C and 700 °C (not shown in Figure 2), was 1.5 %, and can be associated to the evaporation of water adsorbed in the surface of the samples from the atmosphere or even some organic groups remaining after the heat-treatment. It is also observed that YAg10 lost about 1.1% less mass than YAg0 due to silver addition. It is not shown here, but it is worth pointing out that the PVP degradation occurs between 400 °C and 550 °C [8, 31, 32].

The DTA curves of YAg0 and YAg10 are quite distinct. Both samples present an endothermic peak at 828 °C which can be associated with the reaction between Y₂Cu₂O₅ and BaCuO₂ forming YBCO [33, 34]. The endothermic peak at 925 °C for YAg0 can be associated with the YBCO crystallization, and it was the temperature chosen to be applied in all samples presented in this study. However, it can be noted that the YBCO begins to crystallize at about 895 °C for YAg10, which means that the silver addition reduced the crystallization temperature by 30 °C (or 3%). The peak at 954 °C presented by YAg10 is associated with the melting of metallic silver [35]. On the other hand, the endothermic peak at 1031 °C for YAg0 is due to a partial melting of YBCO and such a peak is shifted to 995 °C (or 3.5%) for YAg10, showing that the silver addition also decreases this temperature [14, 36, 37].

Based on the thermogravimetric analysis of Figure 2 and on the literature [5, 8, 31, 32], the samples were firstly heat-treated at 600 °C to ensure the total decomposition of the PVP. Figure 3 shows SEM images of the produced samples. All of which present a fabric-like structure with randomly entangled wires, however, it can be seen that beads are distributed along those wires. This is probably due to water from the acid–base reaction in the precursor solution synthesis. Besides that, the wires are long and smooth. Table 2 shows the average diameter (d_av) of the samples. Wires in the size range 180 nm to 233 nm were found in the samples. No clear relationship was found between d_av and the content of silver present in the system.
After the sintering process at 925 °C, the silver samples shrunk, producing a granular porous-like structure. The shrinkage of the samples is shown in Figure 4(a) and (b). The scale bars within those images are an approximation for comparison purposes. Figure 4(c) shows that, while the Ag-free sample YAg0 maintains its fiber-like structure, the Ag-added samples showed considerable enhancement in density, as shown in Figure 4 from panels (d) to (f). With the wires closer to each other, the grains begin to coalesce during the sintering process and the samples acquire a porous-like morphology. Some works report that the heat-treatment temperatures can be reduced with Ag addition in YBCO bulks [14, 36, 37] due to enhanced heat diffusion. In the case of the present work, the presence of Ag facilitates improved heat-diffusion between the ceramic grains, decreasing the sintering temperature of the samples.

Figure 5 shows XRD diffractograms of all the samples currently studied where it can be seen that the BaCuO₂ phase is present within each of them. Since samples that were produced using PVP of 360,000 g mol⁻¹ instead of 1300,000 g mol⁻¹ contain a pure phase [5], we believe that a longer polymer chain could influence the ceramic phase formation. Such a study will be published in future. As the silver content increases, the intensity of the silver peaks (at around 38° and 49°) also increases. The most intense YBCO peak position shifts with the silver addition, being at 2θ = 32.88°, 32.96°, 32.92°, and 32.98°, for YAg0, YAg10, YAg20, and YAg30, respectively. This can indicate that there is some saturation for silver doping above which metallic silver begins to form along the sample [27]. The peaks around 2θ = 38.3° and 44.5° were identified as characteristic of metallic silver, and their intensity increases with increasing Ag content.

4. Conclusions

In the present work we report the synthesis of YBCO-Ag nanowires via solution blow spinning SBS technique. This approach is based on an acetate chemical route where yttrium, barium, copper and silver acetates were dissolved in a solution with propionic acid (12 wt%), methanol (61.5 wt%), and ammonium hydroxide (26.5 wt%). The silver was added in amounts of 10 wt%, 20 wt%, and 30 wt%. Thermogravimetric analysis show that the addition of silver decreases both the YBCO crystallization and the partial melting temperatures by 30 °C. Both DTA and XRD characterizations showed the presence of metallic silver. Another interesting influence of silver in such complex ceramics is the huge densification of the samples sintered at 925 °C for one hour. SEM images show that the fabric-like morphology of the samples heat-treated at 600 °C is lost with the sintering process, for which a porous-like morphology takes place due to a shrinkage of the ceramic wire network. Thus, the routine described in this study could be used to produce high density bulk superconductors for use in applications such as flywheels, trapped magnets, motors and generators.

| Sample   | \(d_{av} \) (nm) | Deviation (nm) |
|----------|------------------|----------------|
| YAg0     | 233              | 77             |
| YAg10    | 180              | 68             |
| YAg20    | 206              | 76             |
| YAg30    | 191              | 63             |

Table 2: Average diameters of the samples heat-treated at 600 °C with their respective deviations.

![Figure 4: (a) Image of the YBCO-Ag after heat-treatment at 600 °C, and panel (b) shows the visible shrinkage of the sample after sintering at 925 °C. (c) SEM images of YAg0 sample showing the formation of the wires network structure. From (d) to (f) are the SEM images of the YAg10, YAg20, and YAg30, respectively, showing a porous-like structure due to shrinkage after the sintering process.](image-url)

![Figure 5: XRD diffractograms of the produced samples. It can be seen that BaCuO₂ is present in all the samples. The main YBCO peak is at 2θ = 32.88°, 32.96°, 32.92°, and 32.98°, for YAg0, YAg10, YAg20, and YAg30, respectively. The metallic silver peaks are those ones at 38.28° and 44.5° for YAg10, 38.22° and 44.4° for YAg20, and 38.3° and 44.48° for YAg30.](image-url)
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References

[1] K. M. Schaubel, A. R. Langhorn, W. P. Creedon, N. W. Johanson, S. Sheynin, R. J. Thome, Development of a superconducting magnet system for the ONR/GA homopolar motor, AIP Conf. Proc. 823 (2006) 1819. DOI: 10.1063/1.2202611
[2] K. S. Han, D. Lodler, T. O. Deppen, L. Zheng, Actively shielded, high field air-core superconducting machines, IEEE Trans. Appl. Supercond. 26 (2016) 98–105. DOI: 10.1109/TASC.2016.2519409
[3] K. S. Han, S. Kalsi, T. Arndt, H. Karmaker, R. Badcock, B. Buckley, T. Haagun, M. Izumi, D. Lodler, J. W. Bray, P. Masson, E. W. Stautner, High power density superconducting rotating machines-development status and technology roadmap, Supercond. Sci. Technol. 30 (2017) 123002. DOI: 10.1088/1361-6668/aa835e
[4] J. H. Durrell, M. D. Ainslie, D. Zhou, P. Vanderbemden, T. Bradshaw, L. Zadorosny, C. L. Carvalho, J. A. Malmonge, L. F. Malmm, Preparation of granular Bi-2212 nanowires by electrospinning,粉体工学と材料制御 3985 (2016) 16230–16234. DOI: 10.1063/1.2202611
[5] M. Rotta, L. Dasilva, Z. Shen, Y. Wang, W. Chen, L. Fei, K. Li, H. L. W. Chan, L. Bing, H. Karmaker, R. Badcock, B. Buckley, T. Haagun, M. Izumi, D. Lodler, J. W. Bray, P. Masson, E. W. Stautner, High power density superconducting rotating machines-development status and technology roadmap, Supercond. Sci. Technol. 30 (2017) 123002. DOI: 10.1088/1361-6668/aa835e
[6] J. H. Durrell, M. D. Ainslie, D. Zhou, P. Vanderbemden, T. Bradshaw, L. Zadorosny, C. L. Carvalho, J. A. Malmonge, L. F. Malmm, Preparation of granular Bi-2212 nanowires by electrospinning,粉体工学と材料制御 3985 (2016) 16230–16234. DOI: 10.1063/1.2202611
[7] S. Reich, I. Felner, Nonrandom ceramic superconductor-metal composites, High field air-core superconducting machines, IEEE Trans. Appl. Supercond. 1 (2001) 936–939. DOI: 10.1109/TASC.2001.955953
[8] K. M. Schaubel, A. R. Langhorn, W. P. Creedon, N. W. Johanson, S. Sheynin, R. J. Thome, Development of a superconducting magnet system for the ONR/GA homopolar motor, AIP Conf. Proc. 823 (2006) 1819. DOI: 10.1063/1.2202611
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10.1016/j.matchemphys.2019.122607

[31] J. Yuh, L. Perez, W. M. Sigmund, J. C. Nino, Sol-gel based synthesis of complex oxide nanofibers, J.Sol-Gel Sci. Technol. 42 (2007) 323–329. DOI: 10.1007/s10971-007-0736-6

[32] E. A. Duarte, N. G. Rudawski, P. A. Quintero, M. W. Meisel, J. C. Nino, Electrospinning of superconducting YBCO nanowires, Supercond. Sci. Technol. 28 (2014) 015006–015012. DOI: 10.1088/0953-2048/28/1/015006

[33] L. C. Pathak, S. K. Mishra, A review on the synthesis of Y–Ba–Cu–oxide powder, Supercond. Sci. Technol. 18 (2005) R67–R89. DOI: 10.1088/0953-2048/18/9/R01

[34] N. A. Kalanda, V. M. Trukhan, S. F. Marenkin, Phase Transformations in the Y₂Cu₂O₅–BaCuO₂ System, Inorganic Materials 38 (2002) 494–497.

[35] S. Kohayashi, S. Yoshizawa, H. Miyairi, H. Nakane, S. Nagaya, Large domain growth of Ag–doped YBaCuO–system superconductor, Materials Science and Engineering: B 53 (1998) 70–74. DOI 10.1016/S0921-5107(97)00304-8

[36] Y. Nakamura, K. Tachibana, H. Fujimoto, Dispersion of silver in the melt grown YBa₂Cuo₅ crystal, Physica C 306 (1998) 259–270. DOI: 10.1016/S0921-4534(98)00368-2

[37] C. Cai, K. Tachibana, H. Fujimoto, Study on single-domain growth of Y₁₋ₓBa₂₋ₓCu₁₋ₓAg system by using Nd123/MgO thin film as seed, Supercond. Sci. Technol. 13 (2000) 698–702. DOI: 10.1088/0953-2048/13/6/314