Partial Melt Processing of High-Tc Bulk Bi-2212 Starting from different Precursor Powders

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Abstract. In the present work, Bi2Sr2CaCu2Ox (Bi-2212) commercial and homemade precursor powders were investigated. Precursors with different nominal compositions were pressed and melt-processed into silver molds, being then heated at 890-920°C, under 1 atm O2. The bulk samples were then slowly cooled and further annealed at 850°C with a subsequent annealing step at 700°C. The properties of the fully processed samples depended strongly on the maximum processing temperature as well as on the precursor powder employed. Fully processed samples exhibited Ic = 84-146 A and Jc = 800-1400 A/cm², at 77 K. The Bi-2212 stoichiometric nominal composition provided the best results. The correlation between the final microstructure and the properties is not clear.

1. Introduction

Although the partial melt-processing of Bi2Sr2CaCu2Ox (Bi-2212) has been intensively studied, there is still a lack of knowledge on the influence of the precursor in the properties of bulk samples [1]. In the partial melting process, the precursor is heated above the 2212 peritectic decomposition temperature, slow-cooled and subsequently annealed. Aside from its nominal composition and purity, other precursor characteristics were supposed to play a less important role in melt-processed samples, since the considerable liquid fractions should promote homogenization and fast diffusion. However, it has been shown that Jc of bulk samples and thick films are strongly influenced by properties such as the size and morphology of the grains, as well as the second phase content of the precursor [1-3].

In the present work, we investigate the partial melt-processing of bulk Bi-2212 starting from different precursors.

2. Experimental

Commercial precursor powders (NEXANS Superconductors, 2005) with nominal compositions Bi12.16Sr1.98Ca0.83Cu1.97Ox (NEX-I) and Bi12.01Sr1.99Ca1.02Cu1.98Ox (NEX-II) were employed. A homemade precursor, with nominal composition Bi2.0Sr2.0Ca1.0Cu2.0Ox (Bi-2.0), was produced by solid-state reaction of a mixture of oxides and carbonates. The precursors were uniaxially pressed under 39 MPA into silver molds measuring 50(L)x5(W)x10(H) mm³, forming blocks containing about 2.5 g of precursor. The obtained blocks were melt-processed following the thermal schedule depicted in figure
1. At 700°C, the atmosphere was changed from 1 atm O₂ to 1 atm N₂. Samples were analyzed by means of DTA, XRD and SEM/EDS. The DC critical current (Ic) was measured by the four-points method (1 µV/cm).

3. Results and Discussion

The homemade and the commercial precursors showed preponderantly the 2212 phase (Fig. 2). The highest fraction of secondary phases was found in the NEX-II commercial precursor, which presented a significant amount of Bi₄Sr₁₁Ca₅Oₓ (91150), besides (Ca,Sr)₁₄Cu₂₄O₄₁ (14:24), which was also found in the NEX-I commercial precursor.

![Thermal schedule of the partial-melting process](image)

**Figure 1.** Thermal schedule of the partial-melting process employed in the present work

**Figure 2.** X-ray diffraction patterns of the Bi-2212 precursors: 2-2212; X - 14:24; ** - 91150
Endothermic reactions with $T_{\text{onset}} = 892^\circ\text{C}$ (NEX-II and Bi-2.0) and $T_{\text{onset}} = 894^\circ\text{C}$ (NEX-I), under 1 atm O$_2$, were revealed by DTA (Fig. 3). Such reactions are related to the peritectic decomposition of the Bi-2212 phase [4]. The Bi-2.0 endothermic reaction is much deeper and broader than the others, suggesting that a considerably higher liquid amount was formed in this precursor, since all DTA samples had approximately the same weight (10 mg).

Figure 4 shows the critical current ($I_c$) of fully processed Bi-2212 blocks, in function of the maximum processing temperature ($T_{\text{max}}$) and the precursor used. The processed blocks presented a cross section of about 10mm$^2$. The highest $J_c$ values attained were: 1330 A/cm$^2$ (NEX-I), 1350 A/cm$^2$ (NEX-II) and 1460 A/cm$^2$ (Bi-2.0).

Figure 3. DTA of the Bi-2212 precursors studied in the present work. Heating rate: 20°C/min. Atmosphere: 1 atm O$_2$
The Ic and Jc values are strongly influenced by T_max (figure 4). Variations of +/- 5°C in T_max can have a strong effect in Ic and Jc. The best results were attained within T_max = 900-910 °C. Below these temperatures, incipient melt occurred in the blocks, leading to insufficient liquid formation, high porosity and Ic = 0 A. Such incipient melting is consistent with the T_onset values found by DTA (Fig. 3). Above the optimum T_max of each precursor, a significative reduction of Ic and Jc can be observed. This may be partially attributed to an increase in Bi volatilization at higher temperatures. The optimum T_max range seems to be not strongly dependent on the nominal composition, which agrees with previous work [3].

Curiously, the best results obtained with the homemade Bi-2.0 precursor were slightly higher than the best Ic and Jc achieved by using the commercial precursors, despite the high quality and homogeneity of the commercial ones. This may be explained by the higher liquid amount generated upon partial melting of Bi-2.0 samples, as suggested by DTA (Fig. 2). On the other hand both NEX-II and Bi-2.0 blocks, which have practically the stoichiometric 2212 nominal composition, presented similar behaviors at T_max = 905-920°C. In comparison with the NEX-I blocks, the NEX-II and Bi-2.0 samples showed a higher tolerance to changes in T_max. Also, Bi-2.0 and NEX-II blocks led to Ic and Jc values higher than the NEX-I blocks, which is consistent with previous works [5] though the stoichiometric composition is not within the 2212 single-phase region [6]. However, in spite of having practically the same nominal composition, NEX-II precursor exhibited a considerably higher second-phase fraction, in comparison with Bi-2.0 precursor. Such difference can have arisen from the fact that very different processing methods were used for each of these precursors, which may also explain the differences between the results achieved with each precursor.

The XRD and SEM/EDS of fully processed blocks revealed mainly 2212, besides Bi$_2$Sr$_{11}$Ca$_5$O$_x$ (91150), Bi$_{2+x}$(Sr,Ca)$_2$CuO$_y$ (Ca-rich Bi-2201) and coarse (Ca,Sr)$_{14}$Cu$_{24}$O$_{41}$ (14:24) precipitates (Fig. 5 and 6). The 14:24 and 9150 phases arise from 2212 peritectic decomposition, while 2201 solidifies congruently from the liquid [6].

Although high fractions of coarse 14:24 are deleterious for current transport, samples with an apparently better microstructure can show low Jc values, due to incomplete peritectic melting and/or low O2 uptaking during the slow cooling step (O2 loss takes place during partial melting) [4], since Tc is a strong function of 2212 oxygen content [7]. The phase balance of the precursor, as well as the phase balance and the microstructure of melt processed samples influence Ic and Jc values. However, the correlation between current transport properties and phase assemblage/microstructure remains not totally clear. High 2212 fractions with fine and homogeneously dispersed second phases are desirable in fully processed samples, but such conditions are not sufficient for achieving high Ic and Jc. On the other hand, the O2 content of 2212 phase seems to be more critical than the phase assemblage and the microstructure.
Figure 5. XRD patterns of melt-processed blocks: 1- 2201; 2- 2212; * - 91150; X-14:24. Silver (Ag) comes from XRD samples preparation, due to the use of Ag molds for melt-processing. Block B: NEX-I / $T_{\text{max}} = 900^\circ\text{C}$; Block G: NEX-II / $T_{\text{max}} = 905^\circ\text{C}$; Block H: Bi-2.0 / $T_{\text{max}} = 905^\circ\text{C}$

Figure 6. MEV/EDS of melt-processed blocks: matrix - 2212; dark-phase: 14:24. Block B: NEX-I / $T_{\text{max}} = 900^\circ\text{C}$; Block G: NEX-II / $T_{\text{max}} = 905^\circ\text{C}$; Block H: Bi-2.0 / $T_{\text{max}} = 905^\circ\text{C}$
4. Conclusions

In the present work, the partial melt-processing of bulk Bi-2212 was investigated. Different precursors were employed. The $I_c$ and $J_c$ values are strongly influenced by $T_{\text{max}}$ and the optimal $T_{\text{max}}$ range seems to be not strongly dependent on the nominal composition. The role of the phase balance of the precursor, as well as the phase balance and the microstructure of melt-processed samples on current transport properties remains not totally clear. However, the $O_2$ content of 2212 phase seems to be more critical to the transport properties than the phase assemblage and the microstructure. All the precursors studied in the present work provided reasonable results for the bulk samples with the dimensions used here. The Bi-2212 stoichiometric composition gave rise to the best results. Further work is needed, in order to elucidate the role of the precursor features in the transport properties of bulk samples.

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