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Relationships Between Processing Temperature and Microstructure in Isothermal Melt Processed Bi-2212 Thick Films

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abstract—The microstructure and phase assemblage of isothermal melt processed (IMP) $Bi_2Sr_2CaCu_2O_y$ (Bi-2212) thick films have been evaluated. Results from compositional analysis and phase identification indicate that the characteristics of the partial melt greatly influence the microstructural and chemical development of the thick films. The highest critical current densities were obtained in films processed below 800°C where the partial melt uniformly coats the substrate without excessive phase segregation.

I. INTRODUCTION

High quality $Bi_2Sr_2CaCu_2O_y$ (Bi-2212) thick films or tapes typically are melt processed in order to achieve a highly textured microstructure capable of sustaining high critical current densities (J_c's) [1][2]. Recently, isothermal melt processing (IMP) of Bi-2212 thick films has been shown to produce high quality films at temperatures below 800°C[3]. IMP takes advantage of a low solidus temperature in reduced oxygen partial pressures[4][5]. A partial melt can be obtained at temperatures as low as 750°C due to the presence of an eutectic at reduced oxygen atmospheres[6]. Increasing the oxygen partial pressure will recrystallize the partial melt. IMP combines the melting and crystallization steps at the same temperature. J_c's of $1.2 \times 10^5 A/cm^2$ were obtained in IMP films processed at 780°C[1]. These films were found to be highly textured and nearly phase pure. In this paper, the various relationships between processing temperature and microstructure of IMP films are presented.

II. EXPERIMENTAL

A slurry of a nominal $Bi_2Sr_2CaCu_2O_y$ glassy powder dispersed in isopropanol was used to coat both sides of a Ag substrate of approximate dimensions 4 mm x 90 mm. ICP analysis of the starting powder revealed a Ca-poor composition of $Bi_{2.09}Sr_{2.03}Ca_{0.78}Cu_{2.11}O_y$. Details related to producing the glassy precursor can be found elsewhere[7]. Precursor films were heated in Ar at 10°C/min to a temperature between 760°C and 860°C and held for one hour. After this step, the gas flow was switched to 10%O_2 (balance Ar) to oxidize the sample and form the Bi-2212 phase. After an additional 15 hours, the samples were cooled at 5°C/min to room temperature.

Characterization was performed by differential thermal analysis (DTA), x-ray diffraction (XRD), scanning electron microscopy with quantitative energy dispersive spectroscopy (SEM/EDS), SQUID magnetometry, and transport

measurements at 4 and 75 K. The critical current (I_c) was determined using an electric field criterion of approximately 0.5 μV/cm. Samples were prepared for microscopy and quantitative analysis by mounting the samples in cross-section and polishing using standard metallographic techniques. The standard for EDS analysis consisted of a glassy precursor of composition $Bi_{2.13}Sr_{1.94}Ca_{0.91}Cu_{2.02}O_y$ [8]. The average thickness of each film was determined by SEM analysis. Typical thicknesses ranged from 10 to 20 μm.

III. RESULTS AND DISCUSSION

Figure 1 contains the measured J_c values plotted against the processing temperature. The highest J_c of 1.2×10^5 A/cm^2 was obtained in an IMP film processed at 780°C. A backscattered electron image (BEI) of this latter film is shown in Figure 2. Note the high degree of texture and small size of the secondary phases. This microstructure is typical of samples isothermally processed around 780°C. As discussed previously [3], there are five distinct processing temperature ranges. These are the temperature range below approximately 770°C, between 770°C and 790°C where the highest J_c films are produced, from 790°C to 840°C, between 840°C and 850°C where J_c increases again, and finally from 860°C up to the melting point of Bi-2212. The purpose here is to examine in greater detail the underlying reasons for the differences in microstructure and superconducting properties.
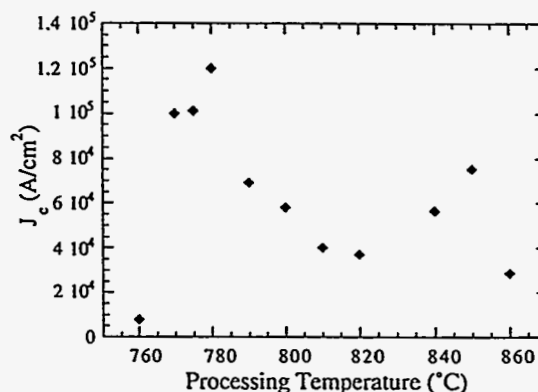
Fig. 1. Critical current density as a function of processing temperature.

Figures 3 contains a micrograph of a film processed at 760°C. The non-planar, ill-defined structure of this film is due to the high viscosity of the partial melt at 760°C; the melt was not able to flow and evenly coat the Ag surface. Large perturbations in the melt surface adversely affect the planar development of the film during crystallization as evidenced by Figure 3. In spite of this, a significant amount of texture exists within the film as shown by the relatively

intense (001) peaks from Bi-2212 and Bi-2201 in the XRD scan in Figure 4.

Fig. 2. BEI cross section of a film processed at 780°C

Fig. 3. BEI cross section of a film processed at 760°C.

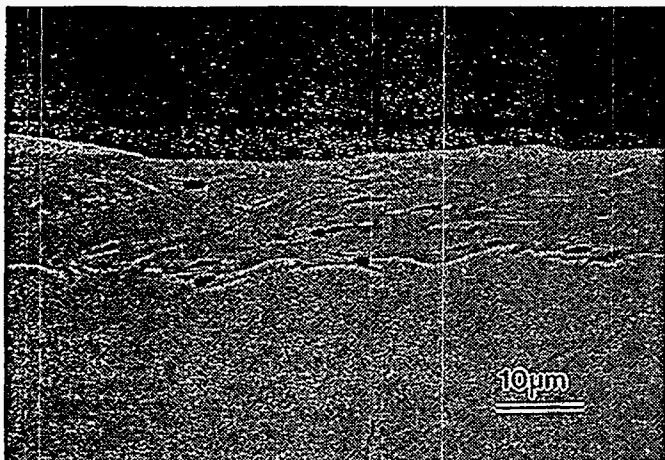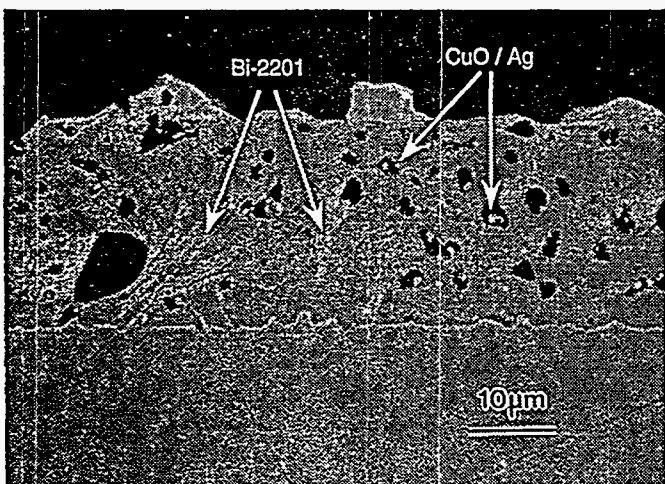EDS analysis of the film grown at 760°C revealed the presence of Ag, CaO, and CuO in addition to Bi-2212 and Bi-2201. The CaO and CuO particles were uniformly distributed throughout the film. Small Ag particles were localized only around the CuO particles in the film. In all other films, the Ag particles that were found were randomly distributed with little apparent microstructural connection to any of other phases. CaO is known to separate out in the melt in inert atmospheres [6]. It is also possible at this temperature that other phases such as Cu_2O, Bi-2201, and $Bi_2Sr_{3-x}Ca_xO_y$ are present in the partial melt as discussed below. The film processed at 760°C was the only one in which CaO and CuO grains were found in abundance. All other films contained $Sr_{1-x}Ca_xCuO_2$ (1:1) and, in a few instances, $Sr_{14-x}Ca_xCu_{24}O_{41}$ (14:24). The CaO found in the film is simply an artifact of the CaO segregation that occurs during melting. CaO is not an equilibrium phase for the starting composition used in this study [9] indicating that the processing temperature was too low for a complete reaction to Bi-2212 to occur. Measurements of the average composition of the Bi-2212 phase and the numerous Bi-2201

grains in the film also reflect the poor reaction kinetics at this temperature. The average composition of the Bi-2212 phase in the film was $Bi_{2.25}Sr_{2.07}Ca_{0.75}Cu_{1.93}O_y$. Bi-2212 grains having appreciable numbers of Bi-2201 intergrowths will deviate from the ideal Cu stoichiometry of 2 (overall composition normalized to 7) [9].
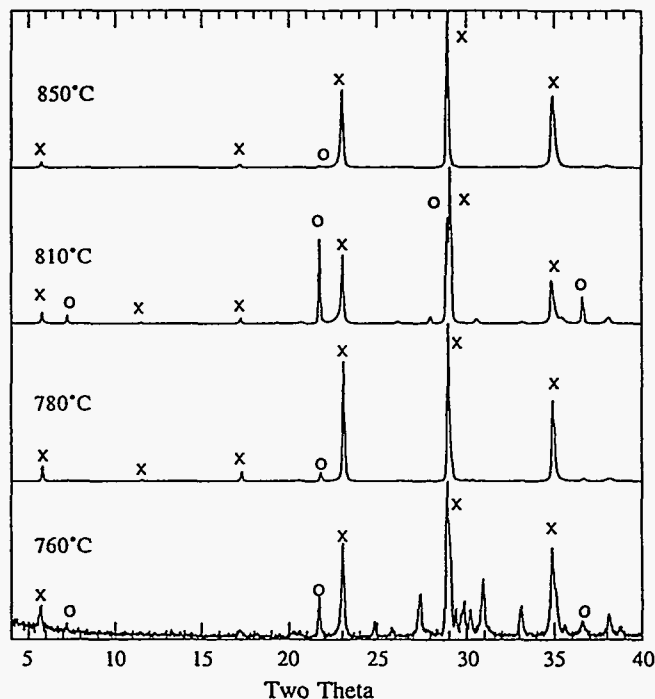

Fig. 4. XRD scans of films processed at 760°C, 780°C, 810°C, and 850°C. The (001) peaks of the Bi-2212 and Bi-2201 phases are marked by x and o respectively.

In the processing region of 770°C to 790°C, the viscosity of the partial melt is high enough to form a uniform layer across the substrate. Crystallization results in a highly textured microstructure free from large grains of the 1:1 or 14:24 phases. This is illustrated the SEM micrograph and XRD scan shown in Figures 2 and 4 respectively of the film processed at 780°C. The average composition of the Bi-2212 phase, $Bi_{2.24}Sr_{1.98}Ca_{0.77}Cu_{2.01}O_y$, indicates that the grains of the superconducting phase were well formed and contained few intergrowths. The presence of some secondary phases is not unexpected since the overall composition, as measured by ICP, lies outside of the solid solution region [9]. In this processing range, both the 1:1 and 14:24 phases were found in the films. The average compositions of these phases were found to be $Sr_{0.58}Ca_{0.41}Cu_{1.0}O_y$ and $Bi_{0.11}Sr_{8.55}Ca_{5.89}Cu_{23.4}O_y$ in the film processed at 780°C. Above 790°C, only the 1:1 alkaline-earth cuprate was found.

Between 790°C and 840°C, the superconducting properties of the films degrade significantly. This effect can be traced to changes that occur in the partial melt. Shown in Figure 5a and 5b are polished cross sections of films melted in Ar at 820°C and 780°C respectively. After one hour, these films were quenched into liquid nitrogen. Figure 5a shows the segregation of CaO particles to the surface of the melt and formation of large grains of the 2:3 Cu-less phase and Bi-

2201. Figure 5b shows a more uniform distribution of Cu_2O, 2:3 Cu-less and Bi-2201. Very few CaO particles were found in the latter film. Note that the microstructures shown in Figure 5 may not represent the exact makeup of the melt at the given temperatures since immersion in liquid N_2 is not necessarily a fast quench[10]. However, the differences between the two quenches are real and lead to pronounced differences in the fully processed films.

The precise oxygen partial pressure at which the eutectic exists is of yet undetermined. Melting in Ar essentially produces an undefined oxygen partial pressure above the film. If too much oxygen diffuses out of the film, the film can recrystallize into a divorced eutectic structure of the 2:3 Cu-less and Cu_2O phases [6]. In effect, the system moves through the eutectic to the oxygen deficient side where the solidus temperature rises up to approximately 820°C [6]. By melting at the higher temperature of 820°C, oxygen diffusion out of the sample is faster. This may explain the coarsening of the 2:3 Cu-less, CaO, and Cu_2O phases shown in Figure 5a. In contrast, the coarsening and segregation effects are much less pronounced in the partial melt at 780°C, presumably due to the higher viscosity of the partial melt at this temperature. Very few CaO particles were found in the film shown in Figure 5b and the 2:3 Cu-less and Cu_2O

phases were evenly distributed and comparable in size. Hence, it is much easier to control the phases and grain sizes present in the melt at the lower processing temperature. This leads to better film performance and phase purity as indicated in Figures 1, 2, and 4 respectively.

For the system to move to the oxygen deficient side of the eutectic is not detrimental to the production of high-quality thick films. Reoxidation will move the system through the eutectic where partial melting will again occur. In fact, it is highly probable that this is exactly the reaction path the films follow when the melting step is carried out in Ar. It is the coarsening of the 2:3 Cu-less and Cu_2O phases and the segregation of CaO in the partial melt that lead to poor film characteristics. During crystallization of the melt, the CaO particles act as nucleation sites for the growth of large alkaline-earth cuprate needles as shown in Figure 6. The coarsening of the 2:3 Cu-less and Cu_2O phases leads to an ill-defined, non-homogenous phase distribution that hampers the reaction kinetics to form Bi-2212 in the temperature range of 790°C to 840°C. For example, the measured composition of the Bi-2212 phase in a film processed at 810°C was $Bi_{2.33}Sr_{2.05}Ca_{0.73}Cu_{1.89}O_y$. The low Cu content of the latter composition is a good indication of poorly formed Bi-2212 grains that contain many Bi-2201 intergrowths [9].
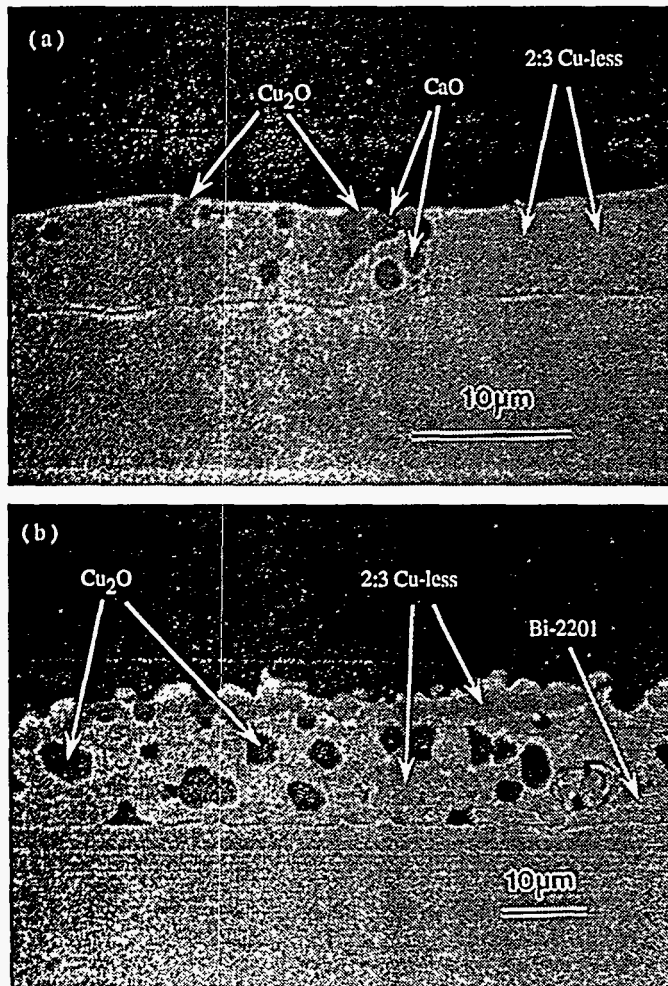

Fig. 5 BEI cross section of films melted in Ar at (a) 820°C and (b) 780°C. After one hour, the films were quenched into liquid N_2.
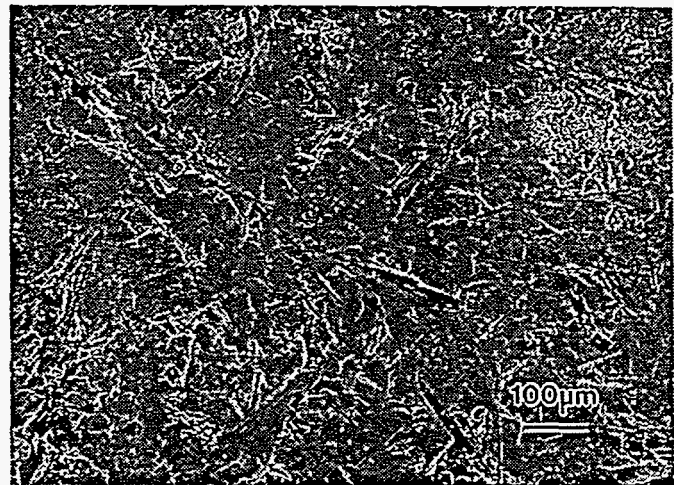

Fig. 6. Secondary electron image of a film produced at 820°C showing the growth of large 1:1 alkaline-earth cuprates.

Between 840°C and 860°C, the J_c values of the films increased again due primarily to the higher processing temperatures. These temperatures are higher then the solidus temperature on the oxygen deficient side of the eutectic. Hence, the partial melt consists of CaO plus a liquid phase. There is no coarsening of the 2:3 Cu-less and Cu_2O phases to lead to an ill-defined phase balance in the film. As a result, a fairly well defined film can be formed with moderate amounts of Bi-2201. For illustration, XRD and SEM results of a film processed at 850°C are shown in Figures 4 and 8 respectively. The XRD results shown a highly textured film with only a small amount of Bi-2201 present. SEM analysis also shows a highly aligned microstructure with some Bi-2201 grains interspersed within. There is also some indication that microcracking is occurring in the film. The average composition of the Bi-2212 grains was

$Bi_{2.18}Sr_{2.05}Ca_{0.77}Cu_{2.00}O_y$. A significant difference in these films, compared to films processed below 800°C, is the coarsening of the microstructure as shown in Figures 2 and 7. Unfortunately, the size of the 1:1 alkaline-earth cuprate needles also increased to about twice the size of those shown in Figure 6. It is believed that these needles result primarily from the segregation of CaO to the surface of the partial melt.
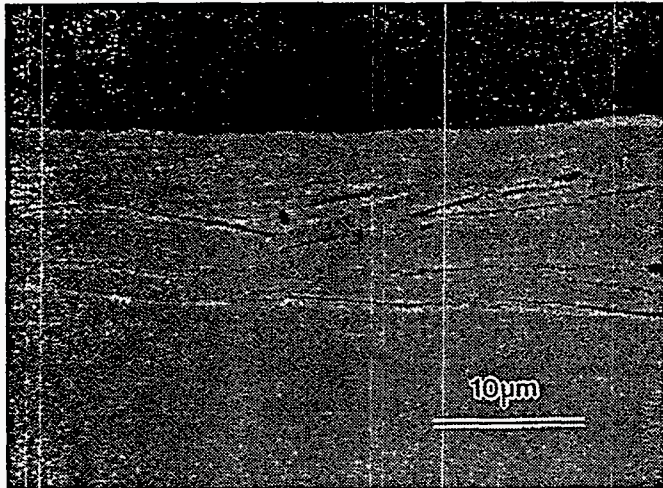

fig. 7. BEI micrograph of a film processed at 850°C

In the processing regime of 860°C and above, coarsening of the microstructure is even more pronounced. Many of the 1:1 needles on the surface of the film processed at 860°C were greater than 500µm in length. Figure 8 contains a cross sectional SEM micrograph of this film. One Bi-2212 grain almost spans the entire thickness of the film. However, as shown in Figure 1, the superconducting properties of this film are not so good. There are a couple of possibilities to account for this. Firstly, the alkaline-earth cuprate needles have coarsened so much as to form a partially connected network with grain sizes comparable to the film thickness. In addition, large grains of Bi-2201 and another secondary phase, $Bi_2Sr_{4-x}Ca_xO_y$ (2:4 Cu-less), were also found in these films with sizes comparable to the film thickness. In
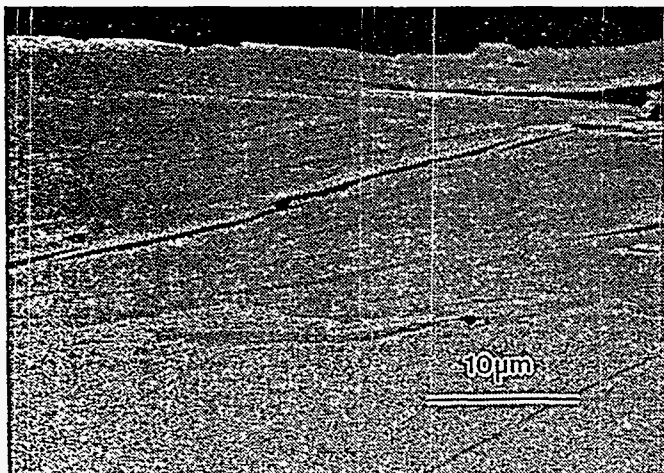

Fig. 8. BEI micrograph of a film processed at 860°C.

short, these secondary phases have grown so large as to limit the number of percolative paths for current flow. The other possibility is the significant amount of microcracking and delamination that is occurring in these films. As shown in Figure 8, a significant network of microcracks exist along the basal planes of the Bi-2212 phase. Note that no such microcracking was seen in the samples processed around 780°C. The reason for this may be due to the smaller size of the Bi-2212 grains in the latter sample. For the case at hand, it is not easy to pinpoint an exact cause for the degradation in Jc above 850°C since both secondary grain growth and microcracking are fundamentally related to the overall coarsening of the microstructure at the higher processing temperatures

IV. SUMMARY

It has been shown that the characteristics of the partial melt greatly influence the formation of Bi-2212 thick films during isothermal melt processing. The best films were grown in the temperature range of 770°C to 790°C with the highest J_c of 1.2×10^5 A/cm^2 obtained in a film processed at 780°C. This latter film was found to highly textured and nearly phase pure. The reason for this stems from the fact that the partial melt formed between 770°C and 790°C was uniform in composition and distribution of phases. At temperatures lower than 770°C, the viscosity of the melt is too high to allow for a uniform melt to coat the surface of the substrate. Above 790°C, the segregation of phases to the surface of the melt, most notably CaO, leads to the formation of large alkaline-earth cuprate needles. From mass balance considerations, the formation of alkaline-earth cuprates necessitates the formation of other Bi-rich secondary phases such as Bi-2201.

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