

1992

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Recommended Citation

Holesinger, T. G.; Miller, D. J.; and Chumbley, L. Scott, "Melt processing of the Bi₂Sr₂CaCu₂O_y superconductor in oxygen and argon atmospheres" (1992). *Materials Science and Engineering Conference Papers, Posters and Presentations*. 51.
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Abstract

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Disciplines

Metallurgy

Comments

This is a manuscript of a proceeding published as Holesinger, T.G., D.J. Miller, and L.S. Chumbley. "Melt processing of the Bi₂Sr₂CaCu₂O_y superconductor in oxygen and argon atmospheres." *INIS* 24, no. 9 (1992): ANL/CP--77532. Posted with permission.

Conf-920802-31

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IN OXYGEN AND ARGON ATMOSPHERES***

ANL/CP--77532

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DE93 002999

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1992 Applied Superconductivity Conference, Chicago, IL, August 24-28, 1992

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Received by OSTI

NOV 16 1992

*Work supported by the National Science Foundation Office of Science and Technology Center for Superconductivity contract #DMR-8809854 (TGH), the U.S. Department of Energy, Division of Basic Energy Sciences-Materials Sciences and Office of Energy Storage and Distribution under contracts #W-31-109-ENG-38 (DJM) and #W-7405-ENG-82 (LSC).

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MELT PROCESSING OF THE $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ SUPERCONDUCTOR IN OXYGEN AND ARGON ATMOSPHERES

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Abstract -- Solidification and subsequent annealing of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (2212) in oxygen and argon atmospheres were investigated in order to identify alternative processing routes for controlling microstructures and superconducting properties. In addition to 2212, several other phases formed on cooling in O_2 and did not disappear upon subsequent annealing. Crystallization in Ar resulted in a divorced eutectic structure of $\text{Bi}_2\text{Sr}_{3-x}\text{Ca}_x\text{O}_y$ and $\text{Cu}_2\text{O}/\text{CuO}$. The superconductor was formed on subsequent anneals. Samples melted in Ar and then annealed generally possessed a more uniform microstructure compared with samples that were melted in oxygen and annealed. Compositional measurements of the 2212 phase suggest that CaO segregation in the melt may be minimized with an overall composition such as $\text{Bi}_{2.15}\text{Sr}_2\text{Ca}_{0.85}\text{Cu}_2\text{O}_y$

INTRODUCTION

It is common to employ a melt-processing step during processing of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (2212) superconductors in order to produce highly aligned microstructures with good superconducting properties.[1] However, phase formation is difficult to control with melt-processing due to the incongruent melting of the 2212 phase. Some of the Sr-Ca-Cu-O phases that form on cooling do not always disappear with subsequent annealing below the peritectic even though they are not the reported equilibrium phases.[2]

It may be possible to circumvent some of these problems through processing in low oxygen partial pressures or altering the starting composition. In general, the melt is oxygen-deficient and the uptake of oxygen during solidification from the melt or crystallization of quenched melts controls the phase formation.[3,4] In the absence of oxygen, the 2212 phase does not crystallize on cooling. Solidification in oxygen or air results in several other phases besides 2212.[5] In addition, annealing steps are generally required after melt-processing and the oxygen partial pressure used here will also affect the phase evolution. It has also been well established that a substantial solid solution region exists for the 2212 phase.[6,7] Therefore, understanding the roles of oxygen and composition during melt-processing is necessary in order to control the microstructure and phase assemblage.

This work supported by the National Science Foundation Office of Science and Technology Center for Superconductivity contract # DMR-88-09854(TGH) and the U.S. Department of Energy, Division of Basic Energy Sciences-Materials Sciences and the Office of Energy Storage and Distribution under contracts #W1-31-109-ENG-38(DJM) and #W-7405-ENG-82 (LSC). Manuscript received August 24, 1992.

In this paper, initial results are presented on phase formation in oxygen and argon during solidification and the recovery of the superconducting phase during subsequent anneals. Several problems associated with melt-processing are examined and possible solutions are discussed based on the results of this study.

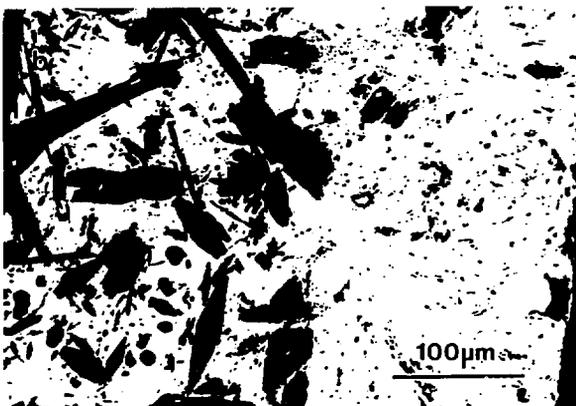
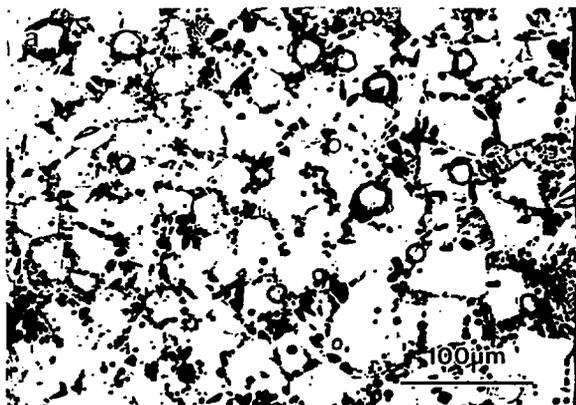
EXPERIMENTAL PROCEDURE

Samples with a nominal composition of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ were prepared from high-purity powders of Bi_2O_3 , SrCO_3 , CaCO_3 , and CuO , mixed in the appropriate ratios, calcined, and splat-quenched to produce a homogeneous starting material. These samples were then ground, pressed into pellets, and annealed at 865°C in oxygen to produce the 2212 phase with minor amounts of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_2\text{O}_y$ (14-24). Pieces of these samples were then melted on MgO single-crystal wafers in oxygen at 1000°C or Ar at 900°C for 15 minutes and cooled at $10^\circ\text{C}/\text{min}$. to room temperature. These samples were also post annealed to study changes in superconducting properties and phase assemblages as a function of oxygen partial pressure. Phase analysis by energy dispersive x-ray (EDS) analysis was performed on polished cross-sections of these melts in a JEOL 840A scanning electron microscope (SEM) using a glass standard as described elsewhere.[8] Melting temperatures as a function of oxygen partial pressure were obtained by differential thermal analysis (DTA) using a heating rate of $2^\circ\text{C}/\text{min}$. Resistivity measurements were obtained using a standard four-probe technique.

RESULTS AND DISCUSSION

A. Solidification in Argon and Oxygen

Major melting events were shown by DTA to occur as a function of oxygen partial pressure at 895°C (100% O_2), 884°C (20% O_2), 869°C (8% O_2) and 801°C (Ar). Hence, the melt processing temperature can be lowered by 100°C in inert atmospheres. Samples for this study were melted on MgO wafers in O_2 at 1000°C and Ar at 900°C . Although these temperatures are higher than normally used during actual processing of wires,[1,2] cooling from the higher temperatures helps to highlight various aspects of the solidification process for easier evaluation. SEM micrographs of polished cross-sections are shown in Fig. 1. Both samples showed a segregation of CaO that accumulated near the top of the melt as well as the presence of some air pockets and pores. Solidification in Ar resulted in a uniform distribution of large, primary crystals of $\text{Bi}_2\text{Sr}_{3-x}\text{Ca}_x\text{O}_y$ (23x) surrounded by a divorced eutectic structure of 23x and $\text{Cu}_2\text{O}/\text{CuO}$, in general



of phases inhomogeneously distributed throughout the sample. The dark needles and particles seen in the top half of this sample in Fig. 1b were identified by EDS as CaO , $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_y$ (1-1), Ca-rich $\text{Sr}_x\text{Ca}_{2-x}\text{CuO}_y$ (2-1), and $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_y$ (14-24). Many of the Sr-Ca-Cu-O needles contained embedded CaO particles. Mixed in among these phases was $\text{Bi}_2\text{Sr}_{4-x}\text{Ca}_x\text{O}_y$ (24x) (gray, block-shaped). Most of the 2212 (gray, needle-like) and 2201 (white, needle-like) phases were confined to the bottom half of the melt. The average composition of the 2212 phase was $\text{Bi}_{2.35}\text{Sr}_{2.15}\text{Ca}_{0.66}\text{Cu}_{1.84}\text{O}_y$. Based on previous work, the high Bi and low Cu contents suggest numerous intergrowths of the 2201 phase within the grains.[6] Mixed in among the 2212 and 2201 phases was a divorced eutectic structure of 22x and $\text{Cu}_2\text{O}/\text{CuO}$ as shown in Fig. 1c. Assuming the melt solidifies from the surface down, this microstructure is consistent with previous works that suggest the Sr-Ca-Cu-O phases form first during solidification which leaves behind a Bi-rich liquid.[4] Hence, the last phases that solidify will be Bi-rich as in the 2201 and 22x phases found in the bottom half of the sample.

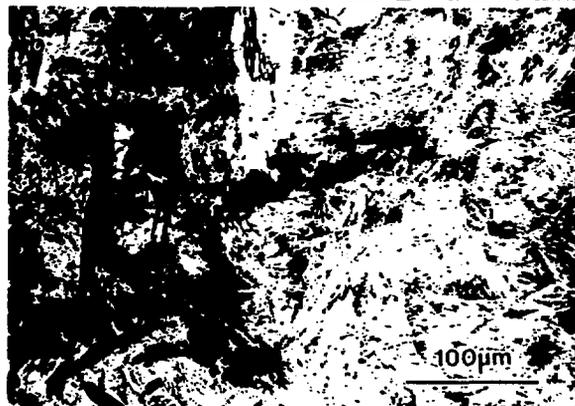


Fig. 1 Backscattered electron micrographs of samples melted in (a) Ar at 900°C and (b) O_2 at 1000°C. The fine eutectic structure found in the O_2 melt is shown in (c). The MgO substrate is located to the right in (a) and (b)

agreement with previous work.[3] Minor amounts of $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_x\text{O}_y$ (22x) and the low-temperature superconductor, $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_x\text{CuO}_y$ (2201) were also found and are probably present to make up for small compositional variations.

In contrast, phase formation upon solidification in oxygen was much more complex resulting in a large number

Fig. 2 Compositional micrographs of 2212 samples initially melted in a) Ar at 900°C and b) O_2 at 1000°C and annealed in O_2 at 850°C. The MgO substrate is located to the right.

These samples were subsequently annealed in O_2 by heating at 10°C/min to 850°C, holding for 100 hours, and finally quenching in air. The resulting microstructures are

shown in Fig.2. SEM analysis revealed only some subtle changes in the sample melted and annealed in O₂. The 1:1 phase was absent and less 2201 was present. On the other hand, none of the original phases in the sample melted in Ar could be found after annealing in O₂ as shown in Fig.2. Phases identified in this sample were 2212, 2201, 14-24, CaO, and 24x. The latter three phases were found predominant in the top half of the sample. Again, many needles of the 14-24 phase contained CaO embedded in them suggesting that CaO may act as a nucleation site for the alkaline-earth cuprates. Overall, the layered microstructure suggests that some partial melting may have occurred during the anneal. However, this sample contains a more uniform microstructure with less of the large alkaline-earth cuprates needles compared to the sample melted in O₂. The average compositions of the 2212 phase in the samples melted in Ar or O₂ and annealed were Bi_{2.18}Sr_{1.96}Ca_{0.85}Cu_{2.02}O_y and Bi_{2.22}Sr_{1.88}Ca_{0.89}Cu_{2.01}O_y respectively. Measured compositions of the secondary phases were also very similar between samples.

Resistivity measurements were performed on the four samples discussed above. The Ar-melted sample was found to be semiconducting. The sample melted in oxygen was superconducting, but with a broad transition and zero resistance at 71K. After the anneal in oxygen, the Ar and O₂-melted samples showed relatively sharp transitions and zero resistance values of 88K and 84K respectively.

B. Oxygen Partial Pressure Anneals

At this point, considerably more effort was directed towards solidification in Ar followed by annealing since this process generally resulted in the same phases and superconducting properties as the O₂-melted samples, but with a more uniform microstructure. Recovery of the 2212 phase was studied as a function of oxygen partial pressure during subsequent anneals. In addition, samples were melted under vacuum and allowed to solidify in Ar in order to reduce the amount of air bubbles trapped in these melts. Finally, the heating rate during anneals was lowered to 2°C/min to better equilibrate the sample with the surrounding atmosphere.

The first anneal of these samples was carried out in O₂ at 850°C for 50 hours. Lowering the heating rate resulted in a somewhat more uniform sample although the microstructure of this sample, shown in Fig. 3a, is similar to that in Fig. 2a. The phases present were the same in either case. The average 2212 composition was Bi_{2.14}Sr_{1.89}Ca_{0.94}Cu_{2.03}O_y.

Samples melted in Ar were also annealed in 20% and 8% O₂ at 840°C and 825°C respectively. In each case, the annealing temperature was approximately 45°C below the melting point for each particular oxygen partial pressure to be consistent with the O₂ anneal at 850°C. The overall microstructure of the sample annealed in 20% O₂ was completely uniform as shown in Fig. 3b. Hence the two-layer microstructure observed in the 100% O₂ anneal may result, in part, from too high of an oxidation rate.[3] The large, dark patches seen in Fig 3b are the 1:1 phase, many of which contained CaO particles, while the smaller needles are the Ca-rich 2:1 phase. Also present were 24x, CuO, 2212, and 2201, but none of the 14-24 phase was found in this sample. The

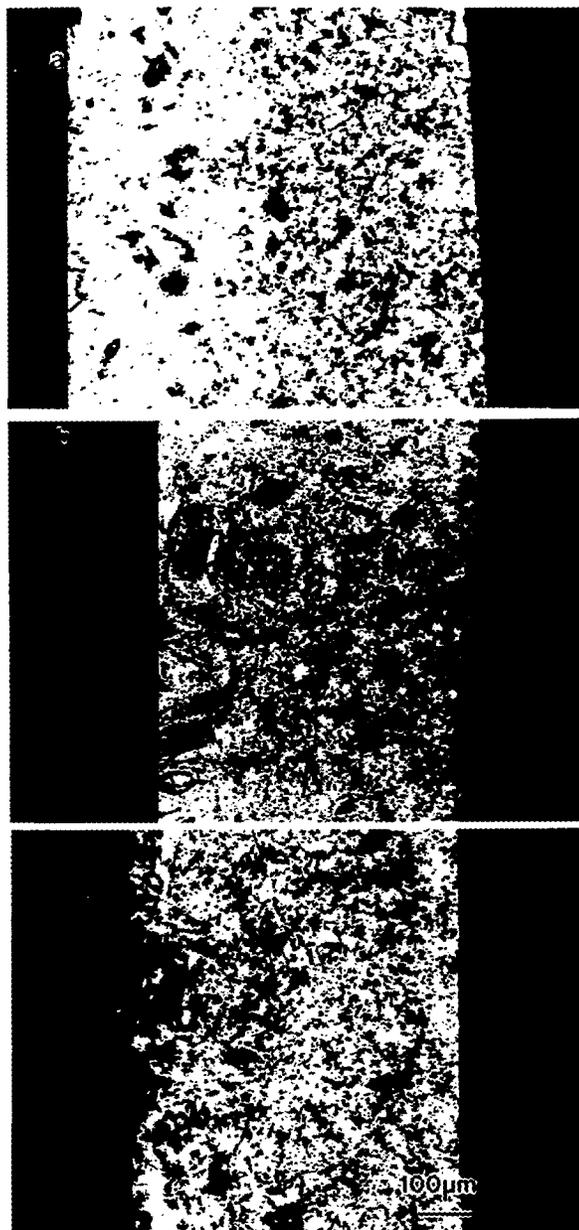


Fig. 3 BEI micrographs of Ar-melted samples annealed in (a) 100% O₂, (b) 20% O₂, and (c) 8% O₂. The MgO substrate is located on the left of each sample.

average composition of the 2212 phase was Bi_{2.16}Sr_{2.03}Ca_{0.84}Cu_{1.97}O_y.

A uniform microstructure was also present after the anneal in 8% O₂ as shown in Fig. 3c. In this case, 23x replaced 24x and considerably more of the Ca-rich 2:1 phase is present compared to the anneal in 20% O₂. The average composition of the 2212 phase from this anneal was Bi_{2.17}Sr_{1.99}Ca_{0.86}Cu_{1.98}O_y.

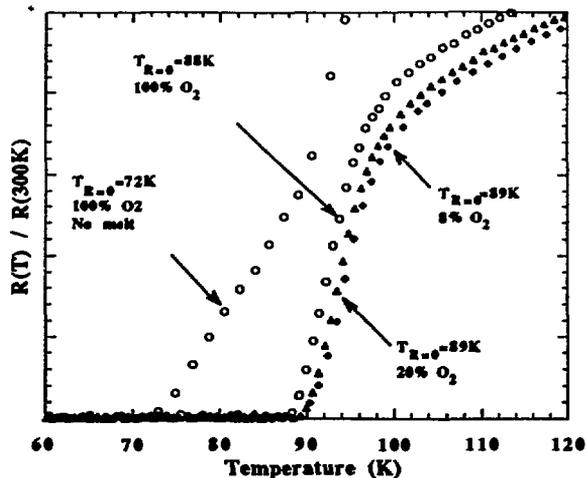


Fig. 4 Normalized resistivity measurements of Ar-melted samples annealed in 100%, 20%, and 8% O₂. For comparison, a 2212 sample annealed without any melting step is also shown.

Resistivity measurements, shown in Fig. 4, revealed all of these samples to be superconducting with zero-resistance measured at 88K for the sample annealed in 100% O₂ and 89K for the other two. Also shown are results from a 2212 sample annealed in O₂ at 850°C without any melting step. The tail seen in this curve is characteristic of such anneals and reflects the benefit of 2212 melt-processing.

From the above results, it is clear that the melting temperatures used may be impractical for normal processing since they exacerbate problems such as CaO separation and the formation of large Sr-Ca-Cu-O needles. However, these experiments are useful in gaining a fundamental understanding of solidification from the melt. For example, melt-processing in inert atmospheres or vacuum is possible since the superconductor can be recovered from the oxygen-deficient phases. Melt processing in reducing atmospheres is especially attractive since the solidus is lowered by approximately 100°C and it appears that the overall microstructure that results after the subsequent anneal can be very uniform provided the sample is carefully annealed in a reduced pressure of oxygen. More work is in progress to refine this process. One area that will be examined is the effect of the microstructure of the Ar-melted sample on phase formation during the subsequent anneal. For example, large grains of 23x may be meta-stable when annealed in a partial pressure of oxygen whereas a fine microstructure of 23x and Cu₂O may completely react to form the 2212 phase.

Separation of CaO can be a problem since it appears that these particles may act as nucleation sites for Sr-Ca-Cu-O phases during solidification or annealing in O₂. Note that only the 14-24 phase is present as a secondary phase in nominal 2212 samples annealed in O₂ without any melting steps.[6,7] The nucleation of alkaline-earth cuprates on the CaO particles will preferentially withdraw material from the sample which

may lead to the formation of other secondary phases, such as 24x, as a mass balance. One possible solution is to substitute more Sr for Ca in the starting material. This seems to be a very practical solution given that the average composition of the 2212 phase in annealed samples was generally deficient in Ca and enriched in Bi. Based on these measured compositions, a logical choice for a starting composition would be Bi_{2.15}Sr₂Ca_{0.85}Cu₂O_y.

SUMMARY

Elements of melt-processing of the Bi₂Sr₂CaCu₂O_y composition in oxygen and argon were investigated in order to study specific problems associated with this process and identify alternative processing routes to circumvent these problems. Solidification in oxygen resulted in significant amounts of other phases in addition to 2212. These other phases did not disappear with subsequent annealing below the peritectic. Crystallization in Ar reduced the number of major phases to Bi₂Sr_{3-x}Ca_xO_y and Cu₂O. However, the superconductor could be recovered from the latter phase assemblage with a suitable anneal in oxygen. The process of solidification in Ar followed by oxygen partial-pressure annealing seemed to result in a more uniform microstructure compared to melting and annealing in O₂. Segregation of CaO occurred in the melt and seemed to act as nucleation sites for alkaline-earth cuprates during solidification or annealing. Compositional analysis of the superconducting phase suggests that an overall composition such as Bi_{2.15}Sr₂Ca_{0.85}Cu₂O_y is a practical alternative to the ideal 2212 stoichiometry to minimize this problem.

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