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ENHANCED SUPERCONDUCTING PROPERTIES IN
 $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ BY THERMAL AND MECHANICAL PROCESSING

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Enhanced Superconducting Properties in $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ by Thermal and Mechanical Processing

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Abstract -- The practical application of high temperature superconductors has been limited by low transport currents in bulk samples. The effect of processing on transition temperature, grain boundary coupling, and flux pinning has been examined for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$. Enhancement of T_c based on composition can be achieved by control of crystallization and subsequent annealing processes while thermo-mechanical processing may be used to modify weak link and flux pinning behavior. The microstructural basis for these changes are related to the composition of the superconducting phase and the presence of defects associated with deformation processing. The implications of these results on conductor development are related to the selection of alloy composition for optimum transition temperature and controlled thermo-mechanical processing which yields a uniform defect structure.

I. INTRODUCTION

The Bi-Sr-Ca-Cu-O system contains several high temperature superconducting phases which are attractive for conductor applications due to their high transition temperature and ease of fabrication. However, there are several well-known limitations to the application of these materials. Firstly, most of the known high temperature superconductors exhibit weak-link behavior at grain boundaries.[1,2,3,4,5] While this poses a serious limitation in terms of conductor applications, this behavior has been exploited by those seeking to develop electronic devices based on SQUIDS produced by this weak coupling at grain boundaries.[6,7] A second limitation is the somewhat low irreversibility line which limits the application of these materials in high magnetic fields at temperatures above $\approx 20\text{K}$. [8] Finally, bulk materials may be limited by relatively poor flux pinning.[3,8] For example, thin films typically exhibit better flux pinning than bulk samples. In the present state of development, this problem seems somewhat less crucial in light of the more serious limitation due to grain boundary weak links. However, a sensible approach in the development of practical conductors should involve parallel studies of each of these issues.

This work addresses some of these issues in the superconducting phase $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$. Although the composition of this phase may vary significantly, it is convenient to refer to this phase according to the ideal "2212" stoichiometry. In spite of recent improvements in the understanding of phase equilibrium and kinetics due to several fundamental studies[9,10,11,12], a number of ambiguities exist

in the literature concerning the solubility limits of the 2212 phase and the maximum transition temperature attainable in this material. For example, the 2212 phase has an approximate transition temperature of 85K, but a number of investigators have reported higher values. Numerous reports have suggested a link between oxygen content and transition temperature, with somewhat higher values of T_c being reported for slight oxygen deficiencies.[13,14,15] Similarly, some investigators have reported variations of T_c with cation stoichiometry.[16,17,18] This work has utilized analytical electron microscopy (AEM) in a systematic study of the 2212 phase to refine the range of solubility for each element and to establish a correlation between T_c and composition of the superconducting phase. In addition, 2212 material has been subjected to thermo-mechanical processing by hot isostatic pressing. The results from this study provide insight into the mechanical deformation of this phase and suggest some mechanisms to improve flux pinning in this material.

II. EXPERIMENTAL PROCEDURES

A series of alloys were prepared in which each element was independently varied from the ideal 2212 stoichiometry. The alloys were prepared by mixing the appropriate ratios of Bi_2O_3 , SrCO_3 , CaCO_3 , and CuO , calcining with intermediate grindings, and finally splat quenching from the melt. In a few instances, calcined powders were cold pressed and sintered without melting and splat quenching. Heat treatments were carried out in a flowing oxygen atmosphere, typically at 865°C for 100 hours. Scanning electron microscopy (SEM) was performed using a JEOL 840A operated at 15 kV while transmission electron microscopy (TEM) was carried out on a Philips CM-30 operated at 100 kV. Each instrument was equipped with an energy dispersive x-ray spectrometer (EDS). Standards for SEM and TEM consisted of a splat quenched amorphous precursor. The $\text{Bi}_2\text{Sr}_{1.7}\text{CaCu}_2\text{O}_y$ powders consolidated by hot isostatic pressing (HIP) were cold-pressed, wrapped in Ag foil, sealed in an evacuated stainless steel can, and then HIPed at 825°C at a pressure of 105 MPa for varying times. Magnetization hysteresis loops and superconducting transition temperatures (T_c) were measured in a dc SQUID magnetometer.

III. RESULTS AND DISCUSSION

Figure 1 shows a plot of measured compositions of the 2212 phase versus nominal alloy stoichiometry for the series $\text{Bi}_2\text{Sr}_2\text{Ca}_{1+x}\text{Cu}_2\text{O}_y$ in which the Ca content was varied by $x=\pm 0.2$, ± 0.5 and $+0.75$ from the ideal value. The compositions were determined by quantitative analysis of EDS spectra collected in the SEM and represent the average of at least 15 measurements. It is immediately apparent that the amount of Ca incorporated into the 2212 phase increases with increasing Ca content in the alloy. The data also

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suggests some decrease in the amount of Sr and Bi contained in the 2212 phase, while the Cu content remains more or less constant. This compositional variation is consistent with the results of other studies. However, due to the penetration and scattering of the electron beam into the sample, this technique is susceptible to fluorescence from nearby or submerged phases. In addition, the 2212 phase generally exhibits intergrowths which may alter the composition somewhat. Therefore, the composition of the 2212 phase was also measured in the TEM, again employing quantitative analysis of EDS spectra. The measurements from the TEM provide greater spatial resolution so that effects from second phases can be avoided. In addition, intergrowths can be identified by imaging the (001) lattice fringes and EDS spectra can be collected from regions which are free of intergrowths. The results of such measurements are shown in Fig. 2.

Fig. 1 Plot of average composition of the 2212 phase versus nominal alloy composition for the series $\text{Bi}_2\text{Sr}_2\text{Ca}_{1+x}\text{Cu}_2\text{O}_y$. The 2212 composition was measured in the SEM by quantitative EDS techniques.

There are several important differences between the data in Fig. 1 and that in Fig. 2. Firstly, the variation in Bi content observed in the TEM measurements is seen to be significantly smaller than that observed in the SEM measurements. Secondly, the decrease in Ca incorporated into the 2212 phase for alloys with a low nominal Ca content is much lower when measured in the TEM. Finally, a very distinct correlation between Ca and Sr contents and a plateau in the interchange between the two elements is observed. The differences between the measurements performed in the TEM and those collected in the SEM can be related to the greater spatial resolution possible in the TEM. In thin TEM foils, electron scatter is significantly reduced compared to bulk SEM samples, so the effect of nearby impurity phases is reduced. In addition, the measurements on these intergrowth-free grains avoid the effect of 2201 intergrowths, which are relatively rich in Bi and relatively depleted of Ca and Cu. Thus, the increase in Bi content and the very low level of Ca content in the SEM measurements of the low Ca samples may be attributed predominantly to the presence of those intergrowths.

Fig. 2 Plot of actual composition of intergrowth-free regions of the 2212 phase versus nominal alloy composition for the series $\text{Bi}_2\text{Sr}_2\text{Ca}_{1+x}\text{Cu}_2\text{O}_y$. The compositions of intergrowth-free regions were measured in the TEM using quantitative EDS techniques.

The above refinement in measurement of the composition of the 2212 phase has allowed a strong correlation to be made between composition and transition temperature. In the case of the alloy series in which either Sr or Ca were varied, an increase in transition temperature could be correlated with an increase in the content of that individual element in the 2212 phase. However, in the case of the alloy series in which Bi or Cu were varied, this relationship did not hold. Rather, it was observed that the transition temperature increased with the total amount of Sr and Ca contained within the 2212 phase, as shown in Fig. 3. In this figure, the transition temperature is plotted versus measured composition of the 2212 phase for each series (i.e. varying Bi, Sr, Ca, and Cu individually). The variation in transition temperature is seen to be independent of the nominal alloy composition but depends very strongly on the particular composition of the 2212 phase. Specifically, it is seen that although all of the compositions measured for the 2212 phase showed a slight excess of Bi and a corresponding deficiency from the ideal values for the sum of Sr and Ca, the transition temperature increases with the total content of Sr and Ca taken together. Given the interplay between Sr and Ca in the compositional measurements, this relationship is not surprising since they behave very similarly in terms of substitutions for one another. In addition, since both elements bond in the +2 oxidation state, their doping behavior is expected to be similar.

In this work, alloys with either a high Sr content or a high Ca content were high in total Sr and Ca content and showed the highest transition temperatures. However, the various compositions behave differently in terms of transformation kinetics and grain boundary characteristics. These differences are illustrated by comparison of $\text{Bi}_2\text{Sr}_{2.2}\text{Ca}_1\text{Cu}_2\text{O}_y$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_{1.5}\text{Cu}_2\text{O}_y$. Each exhibited a sharp decrease in diamagnetic response corresponding to a T_c of the 2212 grains

Fig. 3 Plot of transition temperature measured by diamagnetic response versus actual composition of the 2212 phase. The compositions of intergrowth-free regions were measured in the TEM using quantitative EDS techniques.

of 92.2K and 93.3K, respectively. However, as shown in Fig. 4, the resistive behavior was very different between the two samples. Plotted on a linear scale, the Ca-rich sample exhibits a decreasing normal state resistance and a single transition near 90K with only a small tail. The resistivity decreased below the sensitivity of measurement (zero-resistance) at 72K. In contrast, the Sr-rich sample shows an increasing normal state resistance, a second dip in the resistive transition, and the broad tail, each suggestive of poor coupling across the grain boundaries. This behavior is an artifact of the macroscopic composition and resultant phase assemblage which leads to poor coupling at the grain boundaries. Similar effects have been noted in alloys in which the total content of Sr plus Ca was held constant, but the ratio between Sr and Ca was varied. In general, excesses of Ca seem to provide enhanced diffusion kinetics, presumably due to the smaller ionic radius of Ca so that, even for samples annealed in the solid state, the resistive transitions are narrower than those observed in samples with higher Sr:Ca ratios. However, samples with the lowest Sr:Ca ratios ($\approx 1:2$) begin to exhibit increasing normal state resistances and broad transitions, similar to those observed in the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ sample in Fig. 4. In addition, it is difficult to avoid precipitation of CaO in samples which are rich in Ca. As a result, alloy selection should be based on a compromise between maximum T_c and optimum phase purity and grain boundary coupling. One composition which seems a reasonable compromise is $\text{Bi}_2\text{Sr}_{1.7}\text{Ca}_{1.2}\text{Cu}_2\text{O}_y$.

In addition to these compositional effects, the resistive behavior of these samples is also affected by the thermal processing sequence. For these splat quenched samples, the resistive transition is observed to improve with increasing annealing time for temperatures below the melting point. However, those samples annealed in the solid state invariably exhibit some resistive tail which results in a decrease of the zero-resistance temperature. Annealing in the partial melting

Fig. 4 Plot of resistive transition for $\text{Bi}_2\text{Sr}_{2.2}\text{Ca}_1\text{Cu}_2\text{O}_y$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_{1.5}\text{Cu}_2\text{O}_y$ annealed at 865°C for 100 hours in flowing oxygen

regime, however, generally improves the resistive transition by significantly reducing the low-resistance tails. Figure 5 shows the resistive transition on a linear scale for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ annealed for 25 hours at 850°C compared to a sample annealed at 875°C. Differential thermal analysis (DTA) suggests that at 875°C the sample exists in a partial melting regime, and the resistive transition for this sample shows a less pronounced tail as a result. The resistivity of the sample annealed at 875°C reached the sensitivity of measurement (zero-resistance) at 81K while the sample annealed at 850°C reached zero-resistance at 70K.

Fig. 5 Plot of resistive transition for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ annealed at 850°C and 875°C.

The modifications described above resulting from compositional variations and/or changes in thermal processing may be utilized to optimize the transition temperature and connectivity of grain boundaries in these materials. However, some limitations may persist due to weak pinning in the bulk superconductor. Typically, some form of thermo-mechanical processing is incorporated in the fabrication of wires in order to achieve a high degree of grain alignment, thereby minimizing the weak link problem. However, it is also possible to improve flux pinning in the bulk superconductor by an appropriate deformation process.[19,20] For example, in 2212 powders which were subjected to hot isostatic pressing, magnetization hysteresis loops were expanded for samples HIPed short times (15 minutes) compared to those HIPed for longer times (120 minutes), as shown in Fig. 6. Based on the low transport critical currents of these samples and the lack of scaling of magnetization hysteresis upon dividing the sample, it can be assumed that the grains are weakly coupled. Thus, the increase in hysteresis is a reflection of improved pinning within the grains. The microstructural basis for this increase was revealed by TEM to be due to a uniform distribution of defects in the sample HIPed for 15 minutes. During the initial stages of densification, a high density of dislocations was generated. After 120 minutes of HIP, however, many of these defects were annihilated by recovery mechanisms, resulting in a decrease in pinning.

Fig. 6 Magnetization hysteresis loops for 2212 samples HIPed for either 15 minutes or 120 minutes.

IV SUMMARY

The compositional basis for an enhanced transition temperature in $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ has been examined by correlating compositional measurements of the superconducting phase with T_c . It is found that T_c increases proportionally with the sum of Sr and Ca. In general, however, the 2212 phase exists with a slight deficiency in the sum of Sr and Ca, and excesses of those elements results in degradation of the resistive transition related to weak coupling

at grain boundaries. Proper compositional control and thermal processing can improve the coupling across grains leading to improved transitions. In addition, controlled deformation processing can result in a uniform distribution of defects which leads to enhanced flux pinning, but continued thermal processing can eliminate those defects and reduce pinning.

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REFERENCES

- 1 D. Dimos, P. Chaudhari, J. Mannhart, Phys. Rev. B, 41 (7), pp. 4038-4049, March, 1990.
- 2 S. Jin, R.B. van Dover, T.H. Tiefel, J.E. Graebner, N.D. Spencer, Appl. Phys. Lett., 58 (8), pp. 868-870, Feb., 1991.
- 3 J.E. Tkaczyk, R.H. Arendt, M.F. Garbaskas, H.R. Hart, K.W. Lay, F.E. Luborsky, Phys. Rev. B, 45 (21), pp. 12506-12511, June, 1992.
- 4 M. Huth, M. Schmitt, H. Adrian, Physica C, 178, pp. 203-212, 1991.
- 5 A.C. Wright, K. Zhang, A. Erbil, Phys. Rev. B, 44 (2), pp. 863-866, July, 1991.
- 6 Ken Daly's paper
- 7 J.S. Martens, V.M. Hietala, T.E. Zipperian, G.A. Vawter, D.S. Ginley, C.P. Tigges, T.A. Plut, G.K.G. Hohenwarter, Appl. Phys. Lett. 60 (8), pp. 1013-1015, February, 1992.
- 8 D.H. Kim, K.E. Gray, R.T. Kampwirth, J.C. Smith, D.S. Richeson, T.J. Marks, J.H. Kang, J. Talvacchio, M. Eddy, Physica C 177, pp. 431-437, 1991.
- 9 T.G. Holesinger, D.J. Miller, L.S. Chumbley, M.J. Kramer, K.W. Dennis, Physica C (submitted, June, 1992).
- 10 B. Hong, T.O. Mason, J. Am. Cer. Soc., 74 (5), pp. 1045-1052, 1991.
- 11 S.J. Golden, T.E. Bloomer, F.F. Lange, A.M. Segadaes, K.J. Vaidya, A.K. Cheetham, J. Am. Cer. Soc., 74 (1), pp. 123-129, 1991.
- 12 M.R. DeGuire, N.P. Bansal, D.E. Farrell, V. Finan, C.J. Kim, B.J. Hills, C.J. Allen, Physica C, 179, pp. 333-345, 1991.
- 13 R.G. Buckley, J.L. Tallon, I.W.M. Brown, M.R. Presland, N.E. Flower, P.W. Gilberd, M. Bowden, N.B. Milestone, Physica C 156, pp. 629-634, 1988.
- 14 D.E. Morris, C.T. Hultgren, A.M. Markelz, J.Y.T. Wei, N.G. Asmar, J.H. Nickel, Phys. Rev. B, 39 (10), pp. 6612-6614, April, 1989.
- 15 J. Zhao, M.S. Seehra, Physica C 159, pp. 639-642, 1989.
- 16 T. Satoh, T. Yoshitake, Y. Kubo, H. Igareshi, Appl. Phys. Lett., 53 (13), pp. 1213-1215, Sept., 1988.
- 17 S. Nomura, T. Yamashita, H. Yoshino, K. Ando, J. Am. Cer. Soc., 74, (10), pp. 2711-2714, 1991.
- 18 A.Q. Pham, M. Hervieu, A. Maignan, C. Michel, J. Provost, B. Raveau, Physica C, 194, pp. 243-252, 1992.
- 19 D.J. Miller, S. Sengupta, D. Shi, J.D. Hettinger, K.E. Gray, A.S. Nash, K.C. Goretta, Appl. Phys. Lett. (submitted, July, 1992).
- 20 K. C. Goretta, D. J. Miller, R. B. Poeppel and A. S. Nash, Mater. Res. Soc. Symp. Proc. 251 (in press, 1992).

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