Phase Formation in Ag-sheathed $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ Tapes Using a One- and Two-Powder Process with and without Ag Additions

R.D. Parrella, Y.S. Sung, and E.E. Hellstrom

Dept. of Materials Science and Engineering, and Applied Superconductivity Center,
University of Wisconsin-Madison, Madison, WI 53706 USA

Abstract—The formation of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ ((Bi,Pb)2223) in Ag-sheathed tapes was compared for two different powder processing techniques. In one technique, a phase assemblage of $(Bi,Pb)_2Sr_2CaCu_2O_8$ ((Bi,Pb)2212), $(Ca,Sr)_2CuO_3$, and CuO was produced in a single powder processed by Aerosol Spray Pyrolysis (ASP). This is called a 1-powder process. In the other technique, the same phase assemblage was produced by mixing a precursor powder composed of (Bi,Pb)2212 with a second precursor powder composed of Ca_2CuO_3 and CuO. (Both of the precursor powders were also processed by ASP.) This is called a 2-powder process. A set of tapes were made by the 1-powder process that contained 1, 5, and 10 wt.% Ag. The tape with 1 wt.% Ag yielded a microstructure of nearly phase pure (Bi,Pb)2223.

I. INTRODUCTION

For fabrication of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ ((Bi,Pb)2223) silver sheathed superconducting tapes, it has been shown that a two-powder process may be essential for achieving tapes of nearly phase pure (Bi,Pb)2223 [1]. This method involves mixing a powder composed mostly of the 2212 phase with a second powder composed of specific non-superconducting phases. Further, there is evidence which indicates that beginning with partially reacted powders (mostly 2212 and non-superconducting phases) can lead to higher values of J_c than beginning with fully-reacted powders (mostly 2223) [2]-[4]. Also, by having a controlled phase assemblage of non-superconducting phases in a starting powder, reproducibility may be more easily achieved in terms of both microstructure and J_c.

The exact role silver plays in the phase evolution is not well understood. But a lowering of the melting temperature [5] and a preference for the superconductor grains to grow along Ag/superconductor interfaces have been observed [6]. Reference [5] reports that Ag additions to precursor powders in amounts ≤ 1.0 wt.% have a strong chemical effect observed by differential thermal analysis (DTA). Further there is evidence that the Ag sheath causes non-uniform melting within the oxide core [7].

We report here on (Bi,Pb)2223 tapes in which the powders were processed by Aerosol Spray Pyrolysis (ASP) [8]. A technique was developed in which a controlled phase assemblage of (Bi,Pb)2212, $(Sr,Ca)_2CuO_3$ (2:1) and CuO was achieved in a single powder processed by ASP [7]. This is called the 1-powder process. A second tape was prepared by the more conventional method of mixing a powder of phase pure (Bi,Pb)2212 with a second powder composed exclusively of Ca_2CuO_3 and CuO. This is called a 2-powder process. These tapes were compared in a quench study. Finally, several tapes

were prepared by the 1-powder ASP process with varying amounts of Ag additions (1-10 wt.%). The goal of using the 1-powder process with Ag additions was to eliminate the need of mixing two separately processed powders and avoid non-uniform melting of the oxide core (both of which may lead to inhomogeneities in the final microstructure), while benefiting from a controlled starting phase assemblage of (Bi,Pb)2212, $(Sr,Ca)_2CuO_3$ and CuO.

II. EXPERIMENTAL

A. Powder and Tape Preparation

Six superconducting tapes were fabricated for this study by the Oxide Powder in Tube (OPIT) method. This required preparation of seven powders. (Table I) All of the powders were processed by ASP. The starting reagents Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO, and Ag powders were dissolved into an aqueous nitric acid solution. The aerosol mist was generated by a 1.65 MHz TDK ultrasonic unit. The reactor temperature was 850°C for all powders except powder P2b which was processed at 900°C. Air was used as the carrier gas.

To decompose residual nitrates and complete forming the desired phases, all of the powders were annealed subsequent to production by ASP. All powders except P2b were annealed at 700-730°C for 32-48 h in flowing N_2 [7]. Powder P2b was annealed at 875°C for 12 h in flowing air.

The nominal cation ratios for all (Bi,Pb)2223 tapes were Bi:Pb:Sr:Ca:Cu=1.8:0.4:1.9:2.0:3.0. Powder P2-0 was made by dry mixing precursor powders P2a and P2b in a mechanical grinder. The nominal cation ratios in P2a which was also used to fabricate the (Bi,Pb)2212 tape (TPb) were Bi:Pb:Sr:Ca:Cu =1.8:0.4:1.9:1.0:2.0. The cation ratios in powder P2b was Ca:Cu = 1:1. The x-ray diffraction (XRD) patterns for the powders used in these tapes is presented in Fig. 1. It should be noted that no Ca_2PbO_4 or 2201 were present in any of the powders as determined by XRD.

The powders were loose packed into Ag tubes and the ends were sealed. The tubes were drawn down to 0.18 cm diameter round wires and subsequently rolled into flat tapes that were 0.02 cm thick and 0.3 cm wide. Samples 3.8 cm long were cut from the tapes for study. All samples were annealed at 700°C for 12 h in N_2 prior to any other heat treatment. This pre-annealing treatment has no effect on the nominal phases present as determined by x-ray diffraction, and it is an effective method to prevent the occurrence of bubbling in short length-samples during the subsequent high temperature heat treatment [7]. The sample ends were sealed immediately after the nitrogen anneal by mechanical means.

TABLE I
DESCRIPTIONS OF OPIT TAPES AND CORRESPONDING POWDERS

Tape	Powder	Phases in Powder	1,2,Precursor[a]	wt.% Ag
TPb	P2a[b]	(Bi,Pb)2212	Precursor	0
-----	P2b	2:1+CuO	Precursor	0
T2-0	P2-0	(Bi,Pb)2212+2:1+CuO	2 (P2a+P2b)	0
T1-0	P1-0	(Bi,Pb)2212+2:1+CuO	1	0
T1-1	P1-1	(Bi,Pb)2212+2:1+CuO+Ag	1	1
T1-5	P1-5	(Bi,Pb)2212+2:1+CuO+Ag	1	5
T1-10	P1-10	(Bi,Pb)2212+2:1+CuO+Ag	1	10

[a]The number 1 refers to the 1-powder process and 2 refers to the 2-powder process in which two "precursor" powders were mixed together. Each of the precursor powders were also processed by ASP.

[b]Powder P2a was mixed with P2b to make powder P2-0 for tape T2-0 but was also used alone for tape TPb.

B. ASP 1- and 2-powder process

Tapes T1-0, T2-0, and TPb were heated treated together in a vertical quench furnace. Tapes T1-0 and T2-0 had identical overall nominal compositions and nominal phase assemblages. The only difference is that for tape T1-0 the controlled phase assemblage was achieved in a single powder; whereas for tape T2-0, the same assemblage was achieved by mixing two precursor powders together. One powder, P2a, was phase pure (Bi,Pb)2212 and the other powder P2b, consisted of Ca_2CuO_3 and CuO. Tape TPb was composed solely of the same (Bi,Pb)2212 powder that went into tape T2-0. The purpose of heat treating tape TPb along with T1-0 and T2-0 was to determine whether the secondary phases that resulted were a consequence of forming 2223 or simply the result of partially melting 2212.

The tapes were heat treated in 7.5% O_2/92.5% Ar over a temperature range of 810-830°C at 5°C intervals. To study the phases present at each reaction temperature, the samples were oil quenched after annealing for 24-96 h. Scanning electron microscopy with an energy dispersive x-ray spectrometer (SEM/EDX) and x-ray diffraction were performed on all samples for phase identification. Electron microprobe analysis (EMPA) was also used to quantitatively determine compositions of individual phases. SEM/EDX was performed

on a JEOL JSM 35C with a Tracor Northern EDX system. X-ray diffraction was performed on a Philips PW 1729 diffractometer (Cu Kα) and a Cameca SX50 was used for microprobe analysis.

In addition to the quench study, some samples of tapes T1-0 and T2-0 were heat treated two times with a uniaxial pressing between treatments. These samples were simultaneously heat treated at 820°C for 48 h and oil quenched. The quenched samples were then pressed at 2 GPa which resulted in tape thicknesses of 0.01 cm. The pressed tapes were then heat treated together at 820°C for 144 h and air quenched. The samples were analyzed by SEM/EDX and XRD.

C. Ag-doped Tapes

To study the effects of Ag in the final microstructure, three additional tapes were prepared by the 1-powder ASP process with varying amounts of Ag added. All of the Ag-doped tapes had the exact same nominal superconductor composition and starting phase assemblage as tapes T1-0 and T2-0. However tapes T1-1, T1-5, and T1-10 contained 1, 5 and 10 wt.% Ag, respectively. It should be emphasized, that the high purity Ag was dissolved in the aqueous nitric acid solution prior to forming the ASP powders. This has two benefits: submicron size Ag precipitates and a very uniform distribution of the precipitates within the resulting powders. X-ray diffraction patterns of the powders used to make the Ag-doped tapes are given in Fig. 2.

As was done with T1-0 and T2-0, tapes T1-1, T1-5, and T1-10 were also heat treated two times with an intermediate pressing of 2 GPa. The only difference is the annealing temperature was 815°C to account for the lowered partial melting temperature caused by the presence of Ag in the matrix.

III. RESULTS

The phases present in quenched tapes T1-0, T2-0 and TPb are presented in Table II. The non-superconducting phases
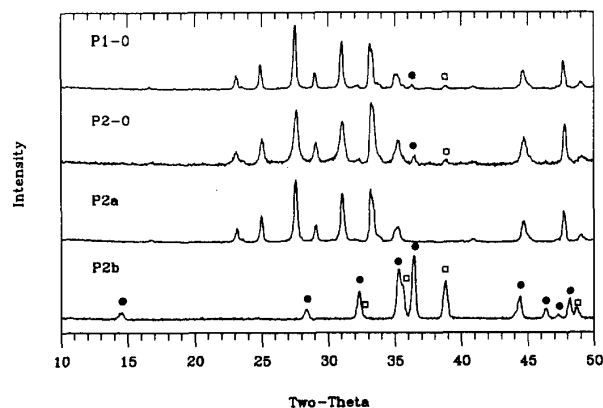

Fig. 1. X-ray diffraction patterns of powders used in tapes for the quench study. Powder P2-0 was formed by mixing P2a and P2b. All peaks belong to (Bi,Pb)2212 except those belonging to 2:1 and CuO denoted by circles and squares respectively.
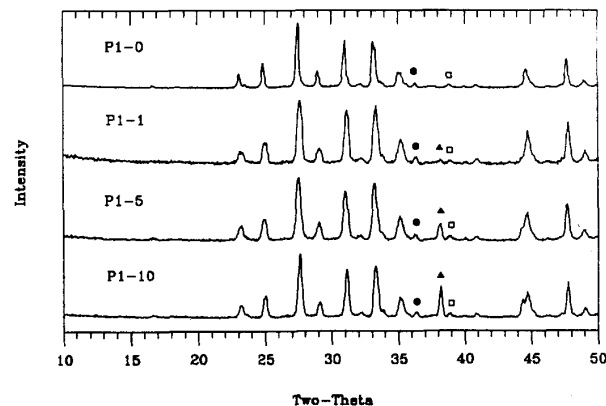

Fig. 2. X-ray diffraction patterns of powders made by the 1-powder ASP process containing 0, 1, 5, and 10 wt.% Ag. All peaks belong to (Bi,Pb)2212 except those representing 2:1, CuO, and Ag phases denoted by circles, squares and triangles respectively.
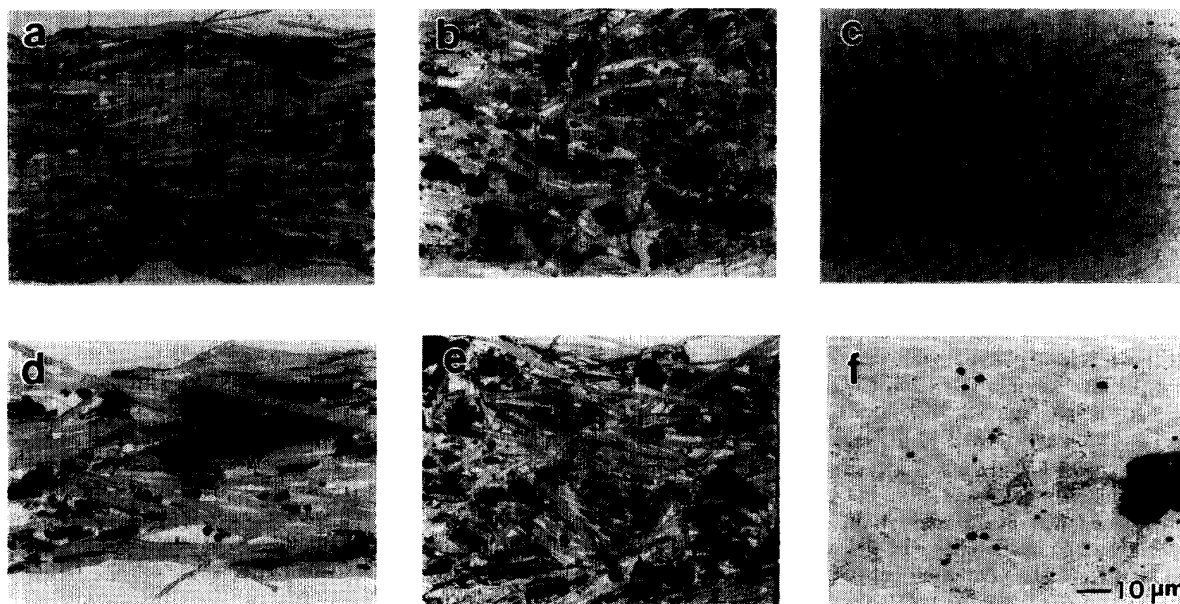
Fig. 3. Backscatter scanning electron micrographs of longitudinal cross-sections of oil quenched tapes (a) T1-0, (b) T2-0, and (c) TPb annealed at 820°C for 96 h. Black phases are 2:1, dark gray phases are mostly CuO and some SrO, the medium gray phase is (Bi,Pb)2223 in (a) and (b) and (Bi,Pb)2212 in (c). The white phase is liquid. Samples from the same respective tapes are shown in (d), (e), and (f) for 825°C. The very large dark phases shown in (d) and (f) are 14:24.
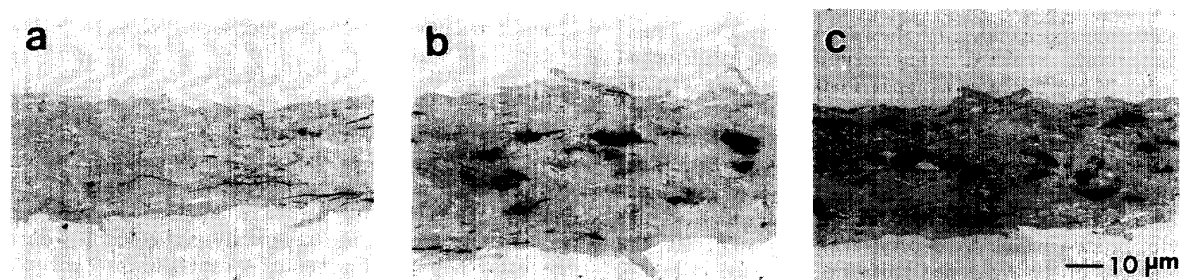

Fig.4. Backscatter scanning electron micrographs of longitudinal cross-sections of (a) T1-1, (b) T1-5, and (c) T1-10 which contained 1, 5, and 10 wt.% Ag respectively and were heat treated twice at 815°C with an intermediate pressing. The black phases are 2:1, and the light gray phases seen in (c) are Ag precipitates. The medium gray phase is (Bi,Pb)2223 and the white phase is liquid.
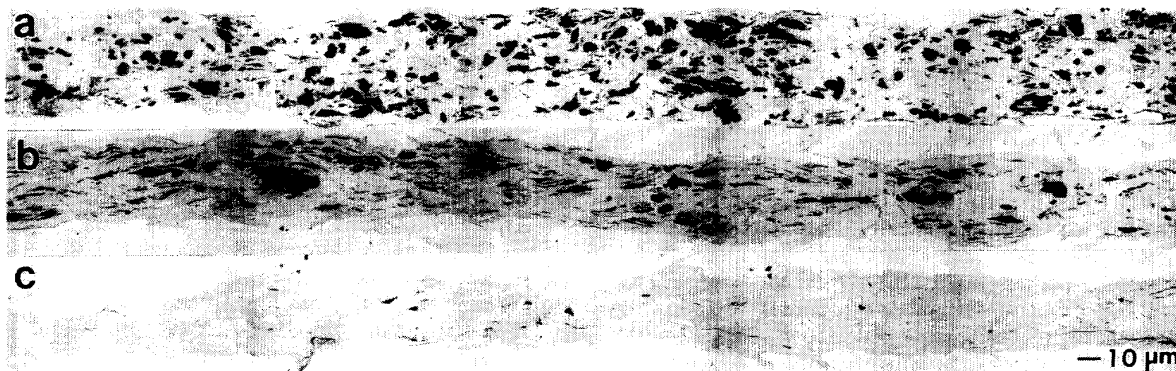

Fig. 5. Backscatter scanning electron micrographs of longitudinal cross-sections of (a) T2-0, (b) T1-0, and (c) T1-1 over a length of 0.58 mm. The difference between the 1- and 2-powder ASP process is clearly evident as well as the effect of Ag doping. All three of these tapes were heat treated twice with an intermediate pressing. Tape T1-1 is nearly phase pure (Bi,Pb)2223, but the presence of liquid is clearly evident in the microstructure.

TABLE II
PHASE RESULTS OF TAPES QUENCHED AFTER 96 HOURS

T (°C)	2:1	CuO	Liquid	14:24	SrO
810	T1,T2 —	T1,T2,TPb	— — —	— — —	T1,T2,TPb
815	T1,T2 —	T1,T2,TPb	T1,T2,TPb	— — —	T1,T2,TPb
820	T1,T2 —	T1,T2,TPb	T1,T2,TPb	— — —	T1,T2,TPb
825	T1,T2 —	— T2 —	T1,T2,TPb	T1 — TPb	T1,T2,TPb
830	T1,T2 —	— T2 —	T1,T2,TPb	T1 — TPb	T1,T2,TPb

present in the oil quenched samples were the same for tapes T1-0 and T2-0 annealed at 810, 815, and 820°C. The solid phases consisted of 2:1, CuO, and SrO. Evidence of a liquid phase first appeared in the 815°C microstructures of both tapes, and was more clearly seen at temperatures ≥820°C. At 825°C the resulting phase assemblage in tapes T1-0 and T2-0 were different. For tape T2-0, 2:1, CuO, SrO and liquid were present in samples quenched at both 825°C and 830°C. For tape T1-0 however, $(Sr,Ca)_{14}Cu_{24}O_{41}$ (14:24) became prominent at 825°C and CuO disappeared. CuO was present in samples quenched at 24 and 48 h, but it no longer existed in samples quenched at 72 and 96 h. At 830°C, the non-superconducting phases in tape T1-0 were 2:1, 14:24, SrO and liquid for all annealing durations between 24 and 96 h.

The XRD pattern of powder P2a used for tape TPb showed no evidence of non-superconducting phases. However, a small amount of CuO and SrO was present in the microstructures for samples quenched at 810, 815, and 820°C. As with the (Bi,Pb)2223 tapes, liquid was first noticed at 815°C and was much more prominent at 820°C. Then at 825°C, as was seen in T1-0, large grains of 14:24 formed and CuO ceased to exist. The same non-superconducting phases (14:24, SrO, and liquid) that were present at 825°C were present for samples quenched at 830°C. Microstructures of tapes T1-0, T2-0, and TPb are presented in Fig. 3.

Samples of T1-0 and T2-0 that were heat treated twice with an intermediate pressing contained 2:1 and some SrO. Tape T2-0 also contained a lot of CuO. The silver doped tapes contained the same non-superconducting phases as T1-0 plus Ag precipitates, which were very large in tape T1-10. The micrographs of the Ag-doped tapes are presented in Fig. 4. Tape T1-1 yielded a microstructure that was virtually phase pure (Bi,Pb)2223 over a considerable length (>0.5 cm) of the sample. Tape T1-5 contained some regions as phase pure but most had some degree of the 2:1 phase present. Tape T1-10 contained a considerable more amount of the non-superconducting phases over its entire length. Fig. 5 illustrates the difference in microstructures between the 1- and 2-powder ASP process and the significant effect of Ag-doping.

IV. DISCUSSION

At 825°C, in the 1-powder (Bi,Pb)2223 tape and the (Bi,Pb)2212 tape a substantial amount of liquid was seen in the microstructures along with the formation of 14:24. However the 2-powder (Bi,Pb)2223 tape did not show evidence of 14:24 at any temperature. We propose the following explanation. Liquid that appears when the (Bi,Pb)2212 phase melts is rich in Bi and Pb, which is evident by its bright white contrast in backscattered scanning electron images and published EDX results on the liquid phase. Some of the

lighter elements then go into forming the 14:24 phase. This is consistent in that EMPA and EDX results performed on 14:24 always yield a Sr:Ca ratio very close to 1:1 and all of the CuO grains are consumed.

Further, EMPA and EDX show that Sr readily substitutes for Ca in Ca_2CuO_3 in the 2-powder tapes. Although the initial phase assemblage is identical in both the 1- and 2-powder tapes, the chemical composition of the individual phases within each powder can vary. The 2:1 in the 2-powder tapes only contains Ca, whereas this same phase in the 1-powder tapes probably contains Sr and Ca. When tapes made with the two types of powder are heated and the (Bi,Pb)2212 begins to melt, in 2-powder tapes, Sr can substitute for Ca in the preexisting 2:1, which we speculate prevents 14:24 from having to form. In tape T2-0, the Sr:Ca ratio in 2:1 increased from 0 to 0.07 in samples quenched from 810°C, and to 0.12 in samples quenched from 830°C. In contrast, we suggest that the preexisting 2:1 in the 1-powder tape already contains Sr. Accordingly, when (Bi,Pb)2212 begins to melt, Sr cannot substitute into 2:1, and we speculate that this causes 14:24 to grow instead. In tape TPb, there was no preexisting 2:1 in the precursor powder, so when it was heated and (Bi,Pb)2212 began to melt, 14:24 formed.

The microstructures show that a uniform distribution of Ag in ASP powder can be very effective at reducing the amount of non-superconducting phases present in the tapes. We believe however, that if too much Ag is added, the large Ag precipitates form and the Ag is no longer distributed uniformly on a fine scale, yielding microstructures with an increased amount of non-superconducting phases.

V. CONCLUSION

A combination of the 1-powder ASP process with as little as 1 wt.% Ag proved to be a successful method for preparing (Bi,Pb)2223 tapes with an extremely high degree of phase purity. We believe the degree of homogeneity resulted from not having to mix two separately processed powders, and inducing non-uniform melting throughout the oxide core by doping the powder with a small amount of evenly distributed Ag particles.

REFERENCES

[1] S. E. Dorris, B. C. Prorok, M. T. Lanagan, S. Sinha, and R. B. Poeppel, *Physica C* 212 (1993) 66-74.
[2] Q. Li, K. Brodersen, H. J. Hjuler, and T. Freltoft, presented at 1992 MRS Fall Conference, Boston, Massachusettts.
[3] Y. Yamada, B. Obst, and R. Flukiger, *Supercond. Sci. Technol.* 4 (1991) 165-171.
[4] M. Mimura, H. Kumakura, K. Togano, and H. Maeda, *Appl. Phys. Lett.* 54 (1989) 1582-1584.
[5] J.-C. Grivel, A. Jeremie, B. Hensel and R. Flukiger, proceedings of the ICMAS conference (1993) 359-364.
[6] Y. Feng, Y. E. High, D. C. Larbalestier, Y. S. Sung, and E. E. Hellstrom, *Appl. Phys. Lett.* 62. (1993) 1553-1555.
[7] Y. S. Sung, E. E. Hellstrom, unpublished.
[8] T. Ward, S. Lyons, T. Kodas, J. Brynestad, D. Kroeger and H. Hsu, *Physica C* 200 (1992) 31-42.