JOURNAL OF MATERIALS SCIENCE **34** (1999) 1619 – 1624

Degradation of BPSCCO superconductors during processing

L. C. PATHAK, S. K. MISHRA
National Metallurgical Laboratory, Jamshedpur 831 007, India
E-mail: suman@csnml.ren.nic.in

D. BHATTACHARYA
Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India

K. L. CHOPRA
Physics Department, Indian Institute of Technology, Delhi 110 016, India

Evaporation losses of Bi, Sr, Cu and Pb during processing of Bi-Pb-Sr-Ca-Cu-oxide (BPSCCO) superconductors were observed, which affected the superconducting properties. Incongruent loss of Bi, Sr, Cu and Pb was reduced by covering the pellets by excess BPSCCO powder during sintering and formation of the 2223 phase was observed to be enhanced. Formation of low temperature eutectic by silver addition was observed to accelerate the rate of evaporation. Lower temperature processing was required for fabrication of high quality Ag sheathed BPSCCO tapes. © *1999 Kluwer Academic Publishers*

1. Introduction

Bi-cuprate superconductor is technologically promising due to its high transition temperature ($T_c = 110$ K) and chemical stability in atmospheric conditions [1]. The formation of $Bi_2Sr_2Ca_2Cu_3O_{10}$ (2223) phase requires the generation of $Bi_2Sr_2Ca_1Cu_2O_8$ (2212) phase which subsequently reacts with CaO and CuO [2]. The rate of 2223 phase formation is slow often requires several days [3–5] and can be speeded up by the addition of Ca_2PbO_4 [6]. Formation of 2223 phase is also dependent on the oxygen partial pressure used during sintering [7, 8]. Formation of homogeneous 2223 phase from a stoichiometric mixture of reactants is often difficult due to evaporation of oxides of Bi, Pb and Cu during sintering [9].

Silver being malleable, ductile and having good conductivities (thermal and electrical) has been widely used for the fabrication of Ag sheathed BPSCCO tapes with high current carrying capacities [10–13]. Systematic investigations of the effect of sintering time on the J_c of Ag cladded BPSCCO tapes and wires reveal that J_c increases initially but it subsequently decreases for longer sintering times [14, 15]. The interaction of Ag with BPSCCO compounds has been studied by several workers [15–21] but with contradictory conclusions. Jin *et al.* [16] have reported that no reaction of Ag with BPSCCO tape occurs if the Ag content in the matrix <20 wt % whereas Dou *et al.* [17] have observed serious deterioration of T_c and J_c in the presence of even lower amounts of Ag under high partial pressure of oxygen. Ag cladded BPSCCO tapes with high J_c values have reportedly been fabricated by processing under low pO_2.

Hwu *et al.* [18] have concluded that reaction of Ag with BPSCCO affected the Sr-O and Bi-O planes, but had no effect on the Cu-O bonds, which is contrary to the XPS results of Lindberg *et al.* [19], who have observed changes in the binding energy of Cu-O at the BPSCCO-Ag interface. Feng *et al.* [20] have observed formation of Bi-2201 with 001 faceting at the interface of Ag cladded 2212 superconductor tapes but Arendt *et al.* [21] could not observe any inter-diffusion or degradation at the interface. It has been suggested that presence of unreacted carbonates in the BPSCCO powders could possibly cause lowering of the liquidus temperature during sintering of the tapes leading to significant drop on J_c and T_c. Lowering of melting point due to formation of low temperature BPSCCO-Ag eutectic has been reported.

In order to develop a universal picture of the effect of sintering conditions on the superconducting properties of BPSCCO powder compacts, BPSCCO-Ag composite and Ag sheathed BPSCCO tapes, we have carried out extensive studies which are reported here.

2. Experimental

2.1. Powder preparation and characterisation

Submicron sized homogeneous $Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_x$ powders were synthesised by the pyrophoric route [22] using $Bi(NO_3)_3$ [99%], $Pb(NO_3)_2$ [99%], $Sr(NO_3)_2$ [99%], $Ca(NO_3)_2{\cdot}2H_2O$ [98%], and $Cu(NO_3)_2{\cdot}3H_2O$ [99.9%] as the starting materials. The Bi : Pb ratio was adjusted to 1.4 : 0.6 so as to obtain a large fraction of 2223 phase in the product [1]. The freshly generated pyrophoric powders were calcined at 1073 K for 6 h in air.

0022–2461 © *1999 Kluwer Academic Publishers*

BPSCCO-Ag$_x$ (x in wt %) composites were prepared by mixing 400 mesh Ag (99.95%) powder thoroughly with the calcined BPSCCO powders. The melting points of BPSCCO-Ag$_x$ powders were obtained from DTA measurement using SHIMADZU DT 30 thermal analyser.

The powders were palletised by biaxially pressing 10 g of calcined powder in a steel die at a pressure of 12.4 MPa.

2.2. Sintering of BPSCCO

BPSCCO pellets prepared from the calcined powders were sintered at 1118 K in air for different soaking periods of 60, 96 and 192 h. The green pellets were sintered under the following conditions:

(a) the green pellets were left uncovered during sintering, and

(b) the samples were covered while sintering by the same calcined powder from which the pellet was fabricated.

BPSCCO-Ag$_x$ ($x = 0$–10 wt %) pellets were sintered either in air or in nitrogen atmosphere at 1118 K for a fixed soaking period of 96 h.

The compositions of all the sintered pellets were investigated by energy dispersive X-ray (EDX) spectroscopy analysis and fracture surfaces of the sintered pellets were studied by scanning electron microscope (SEM). EDX analysis gives the chemical composition of the surface of the samples, where the depth of X-ray emission is of the order of a few micro-meter and varies with the elements present in the samples. In order to get the true picture about the chemical composition, the samples were bisected and large area scanning was made to acquire the bulk analyses of the samples. Apparent densities (which include the pores and voids) of all the sintered pellets were measured using Archimedes principle with an accuracy of 2% by liquid immersion technique. Phases of the sintered pellets were analysed by X-ray diffraction (XRD) technique.

2.3. Fabrication of Ag sheathed tapes

The Ag sheathed BPSCCO tapes were prepared using the powder in tube (PIT) method. In this method, silver tubes filled with BPSCCO powder were swaged, rolled or drawn and then heat treated at elevated temperatures. Two types of starting materials and sintering conditions for the fabricated tapes were used:

(a) Ag sheathed tapes were fabricated using calcined powder which was principally composed of 2212 phase. The sheathed tapes were sintered at 1118 K in air for different soaking periods of 10, 30 and 96 h, and

(b) Ag sheathed tapes were fabricated using powders obtained by grinding pellets which had high concentration of 2223 phase ($>50\%$). These Ag sheathed tapes were sintered either at 1118 K or at 1093 K in air for different soaking periods. Ac susceptibilities of the fabricated tape were investigated to assess the relative amount of superconducting phases formed after various processing steps.

3. Results and discussion

3.1. Effect of sintering time

Ac susceptibility measurements indicate that BPSCCO pellets sintered without powder cover suffered progressive loss of the 2223 phase content as the sintering time at 1118 K was increased from 60 to 192 h. EDX analysis revealed that the pellets became progressively deficient in Bi, Pb, and Sr with concomitant formation of non-superconducting phases as observed from X-ray diffraction analysis. The apparent densities of the pellets were also decreased progressively. When powder encased green BPSCCO pellets were sintered, the 2223 phase content and density of the sintered pellet increased with increasing sintering time at 1118 K. The Table I summarises the observed properties of the pellets sintered with and without powder cover. The observed variation of densities is possibly due to these following factors:

TABLE I Phase and composition analysis of BPSCCO pellets sintered at 1118 K for different soaking time with and without powder cover. The elemental composition was normalised by setting the relative content of Ca to 2.00 and oxygen content is calculated on the basis of valence of the cations

Sample condition and sintering times	Initial composition	Final composition	%Total superconducting phase measured by Ac susceptibility	%2223 Phase measured by Ac susceptibility	Density (g cm^{-3})	Phases analysed by XRD
Without covering 60 h	$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_{10}$	$Bi_{1.28}Pb_{0.51}Sr_{1.17}Ca_2Cu_{2.32}O_{7.92}$	54	30	4.5	2223 + 2212 + Ca-CuO
Without covering 96 h	$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_{10}$	$Bi_{0.56}Pb_{0.22}Sr_{0.84}Ca_2Cu_{2.40}O_{6.30}$	43	18	4.5	2223 + 2212 + Ca-CuO
Without covering 192 h	$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_{10}$	$Bi_{0.35}Pb_{0.22}Sr_{0.55}Ca_2Cu_{2.35}O_{5.64}$	40	0	4.1	2223 + Ca-CuO
With covering 60 h	$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_{10}$	$Bi_{1.33}Pb_{0.56}Sr_{1.38}Ca_2Cu_{3.04}O_{8.97}$	56	31	4.5	2223 + 2212
With covering 96 h	$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_{10}$	$Bi_{1.21}Pb_{0.56}Sr_{1.36}Ca_2Cu_3O_{8.73}$	58	40	5.0	2223 + 2212
With covering 192 h	$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_{10}$	$Bi_{1.06}Pb_{0.54}Sr_{1.36}Ca_2Cu_3O_{8.49}$	62	51	5.2	2223 + 2212

(a) formation of low density phases due to degradation during sintering, which is also been confirmed from the XRD analyses,

(b) increased volumes of pores and voids due to evaporation of materials from the samples during sintering, and

(c) decrease of high T_c i.e. 2223 phase formation during sintering.

SEM analysis of the fractured surfaces of the two types of pellets showed large platelet type of grain growth for pellets sintered with powder cover (Fig. 1a) and crystalline rod shaped growth of grains are observed in the uncovered samples. EDX analyses revealed that more Ca rich grains are formed in these uncovered samples whereas, the compositions of the powder covered grains are more or less uniform.

3.2. Effect of silver on sinterability of BPSCCO

DTA analysis of BPSCCO-Ag$_x$ samples (Fig. 2) show that the melting point decreased with the addition of increasing amounts of Ag. This lowering of melting point may possibly be accounted for by the following:

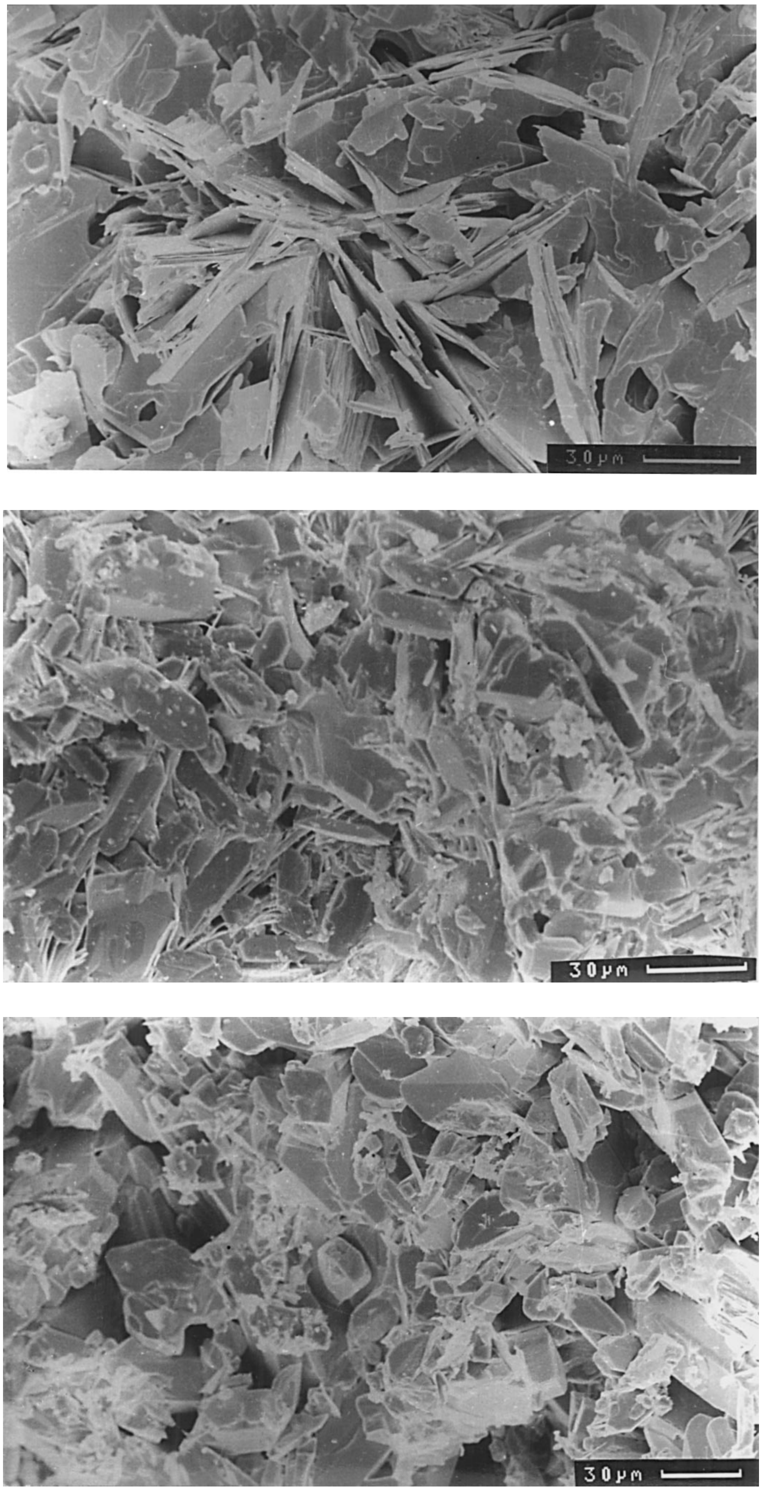

Figure 1 SEM of BPSCCO pellets sintered 1118 K: (a) for 192 h with powder covering (b) for 192 h without powder covering (c) for 96 h with Ag (2 wt %).

TABLE II Composition analyses of BPSCCO-Ag pellets sintered in air at 1118 K for 96 h. The elemental composition was normalised by setting the relative content of Ca to 2.00 and oxygen content is calculated on the basis of valence of the cations

Silver concentration (wt %)	Initial composition	Final composition	Melting peak (K)	%2223 phase measured by Ac susceptibility	Density (g cm^{-3})	Phases analysed by XRD
0	$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_{10}$	$Bi_{1.33}Pb_{0.56}Sr_{1.36}Ca_2Cu_3O_{8.9}$	1138	45	5.08	2223 + 2212
1	$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_{10}$	$Bi_{0.73}Pb_{0.33}Sr_{0.80}Ca_2Cu_{1.92}O_{6.05}$	1134	20	5.32	2212 + 2223 + Ca-CuO
2	$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_{10}$	$Bi_{0.59}Pb_{0.25}Sr_{0.73}Ca_2Cu_{1.71}O_{5.58}$	1126	5	4.5	2212 + 2223 + Ca-CuO
5	$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_{10}$	$Bi_{0.21}Pb_{0.09}Sr_{0.32}Ca_2Cu_{1.33}O_{3.74}$	1110	0	4.2	2112 + Ca-CuO
10	$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_{10}$	$Bi_{0.19}Pb_{0.0}Sr_{0.27}Ca_2Cu_{1.12}O_{3.68}$	1093	0	4.0	2212 + 2201 + Ca-CuO

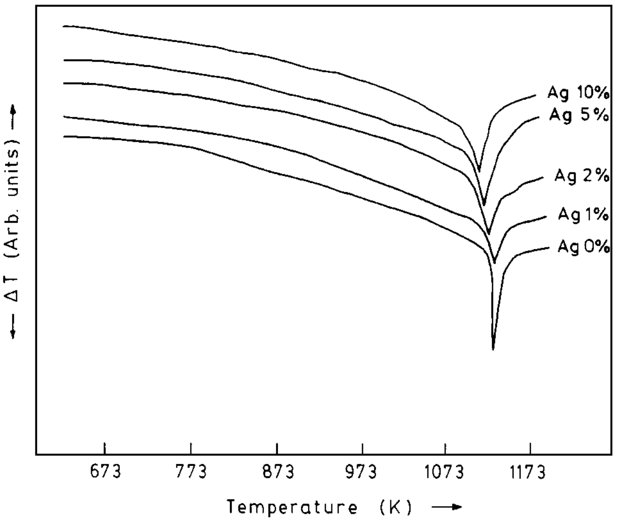

Figure 2 DTA of BPSCCO-Ag$_x$ ($x =$ wt %) powders (in air).

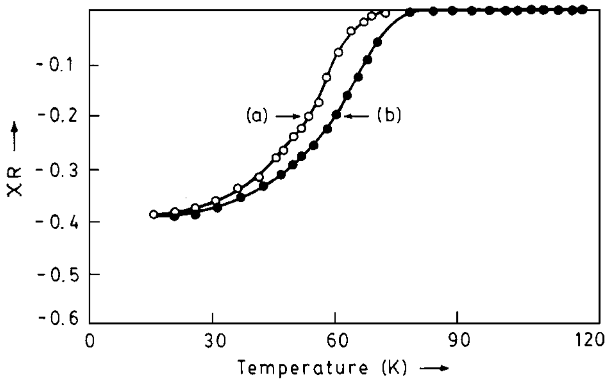

Figure 3 AC susceptibility of BPSCCO powder compact sintered at 1118 K for 96 h in (a) air and (b) after annealing in N_2 of sample (a).

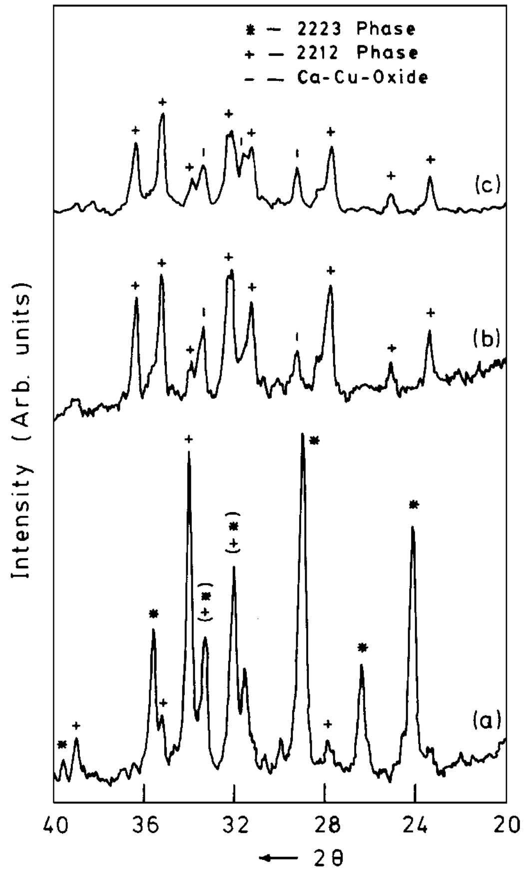

Figure 4 XRD of the pellets of: (a) BPSCCO—sintered for 192 h at 1118 K with covering, (b) BPSCCO—sintered for 192 h at 1118 K without covering and (c) BPSCCO—Ag (2 wt %)—sintered for 96 h at 1118 K.

(a) Metallic silver has been known to cause partial reduction of CuO to Cu_2O. Cu_2O forms a eutectic with PbO [23], and

(b) Ag-O-CuO-Cu_2O-PbO forms a low melting eutectic [24].

The formation of these low melting eutectics also causes significant loss of various cations excluding CaO at the sintering temperature, possibly through evaporation, as can be seen from Table II. The composition of the pellets has been determined by EDX analysis and the average value of the composition determined at various points has been reported.

Ac susceptibility measurements (Fig. 3) and X-ray diffraction analysis (Fig. 4c) indicate that, on sintering of the silver containing samples at 1118 K for 96 h, a drastic decrease in the formation of 2223 phase occurs. Fig. 1c (SEM of BPSCCO-Ag_2 pellet) shows that platelet nature of growth, observed in BPSCCO samples as reported earlier (Fig. 1a and b), was absent. The onset superconducting transition of BPSCCO-Ag_5 (Fig. 3a) was at 75 K which is lower than 80 K of 2212 phase. The same superconducting sample showed transition at 80 K after annealing in nitrogen atmosphere (Fig. 3b). The lowering of T_c to 75 K was possibly due to excess oxygenation of the samples leading to increased oxygen content in Bi-O plane [25] on account of oxygen desorption by silver.

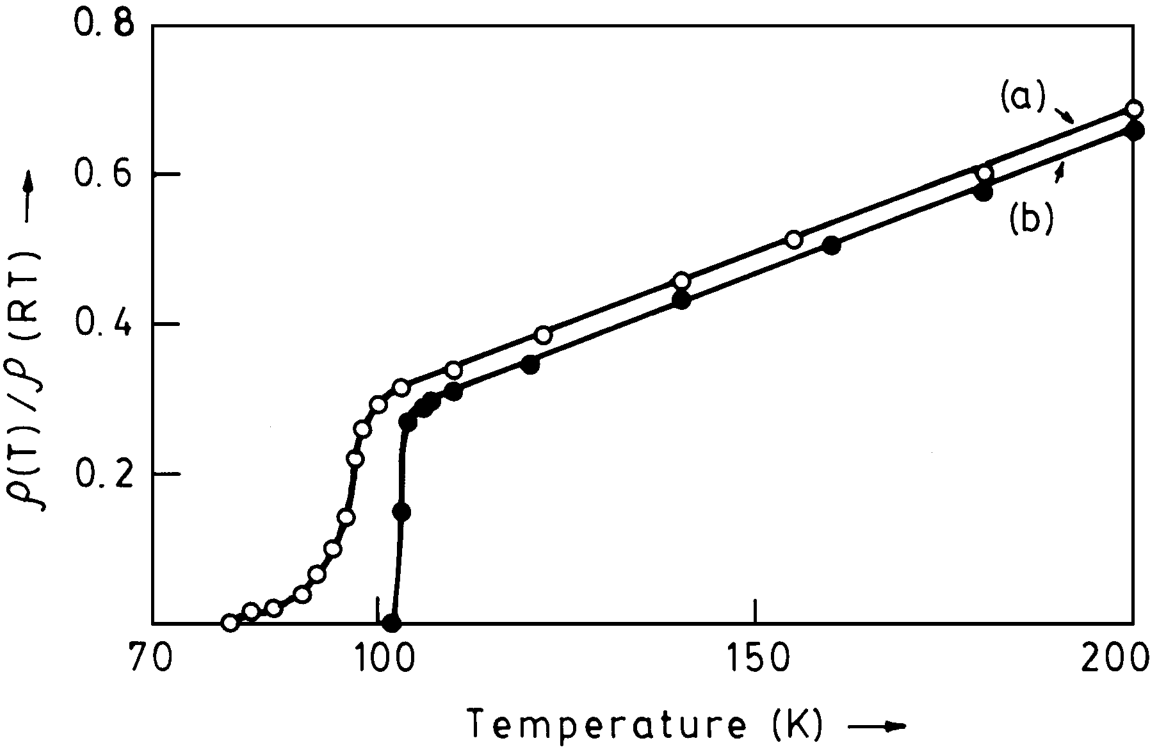

Figure 5 Resistivity of Ag sheathed tapes, sintered at 1118 K for 10 h in air, fabricated from (a) as calcined powder (b) powder with more than 50% 2223 phase.

3.3. Fabrication of Ag sheathed tapes

Ag sheathed tapes fabricated from the as calcined BPSCCO powder when sintered in air at 1118 K for different soaking periods of 10, 30 and 96 h exhibited zero Resistivity at 80 K (Fig. 5a), whereas the Ag sheathed tapes made from BPSCCO powders having greater than 50% 2223 phase and sintered at the same sintering temperature of 1118 K for 10 h had T_c at 102 K (Fig. 5b) with J_c value of 198 A/cm^2 at 77 K. The same samples sintered at 1118 K for longer soaking periods of 30 and 96 h showed degradation of the superconducting properties. This observation suggests that a low temperature processing is necessary to prepare high current carrying superconductors.

The Ag sheathed tapes, fabricated from BPSCCO powders with >50% 2223 phase, and sintered at 1093 K (and soaked there for 10 h) had a J_c value of 90000 A/cm^2 at 15 K with a $T_c(0)$ at 102 K. From the Ac susceptibility measurements it has been observed that the 2223 phase decreases with both the sintering time and temperature. At high temperatures the rate of decrease of 2223 phase is more. For instance, a decrease of 23, 52 and 100% of the 2223 phase is observed in the samples sintered at 1118 K for 10, 30 and 96 h respectively. Whereas, only 8% decrease is observed in the tapes sintered at 1093 K for 10 h.

On further increase of sintering time the J_c values of the sintered tapes are decreased without affecting the $T_c(0)$. It has been inferred from X-ray diffraction analysis of BPSCCO layers (obtained after peeling off the covering Ag layer) that the decrease of critical current density observed on sintering for long lengths of time was due to formation of 2212 and Ca-Cu-oxide as a result of interaction of Ag with BPSCCO at the interface. Silver diffuses considerably into BPSCCO [26] and as a result superconducting properties of the Ag sheathed tapes are affected on prolonged heating.

4. Conclusion

1. Evaporation of Bi, Sr and Pb has been observed while processing BPSCCO superconductors which is in agreement with other reports [9, 27]. Evaporation can be minimised by increasing the vapour pressure of the constituents inside the furnace during sintering; we have achieved it by covering the pellets with the same powder of BPSCCO during sintering.

2. Presence of Ag in BPSCCO matrix lowers the melting point and hence enhances the rate of evaporation. However, contrary to reports, this lowering of melting point is due to a redox reaction between CuO-PbO-Ag which leads to formation of a eutectic which melts at about 973 K [23].

3. Since there is extensive inter-reaction between Ag cladding and BPSCCO at the interface the sintering time should be optimised.

4. It has been observed that the Ag sheathed tapes should be fabricated from the BPSCCO pellets having high concentration (>50%) of 2223 phase and sintered for short duration at lower temperature with respect to the pellets to achieve better superconducting specimens.

References

1a. B. GOGIA, S. C. KASHYAP, D. K. PANDYA and K. L. CHOPRA, *Solid State Commun.* **73** (1990) 573.
1b. B. GOGIA, S. C. KASHYAP, D. K. PANDYA and K. L. CHOPRA, *Bull. Mater. Sci.* **14** (1991) 217.

1c. D. K. PANDYA, B. GOGIA, S. C. KASHYAP and K. L. CHOPRA, in Proc. International Conf. on high T_c Superconductors, (BHTSC'89), 1989, p. 210.
2. W. ZHU and P. S. NICHOLSON, *Appl. Phys. Lett.* **61** (1992) 717.
3. H. SASAKURA, S. M. NOAMIGAWA, K. NAHIGASHI, M. KAGACHI, S. NAKANISHI, N. FUKUOKAWA, S. NOGUCHI, K. OKUDA and A. YANASE, *Jpn. J. Appl. Phys.* **28** (1989) L1163.
4. K. H. SANDHAGE, G. N. RILEY JR. and W. L. CARTER, *J. Metals* **3** (1991) 21.
5. S. KOYAMA, U. ENDO and T. KAWAI, *Jpn. J. Appl. Phys.* **27** (1988) L1861.
6. F. H. CHEN, H. S. KOO and T. Y. TSENG, *Appl. Phys. Lett.* **58** (1991) 637.
7. U. ENDO, S. KOYAMA and T. KAWAI, *Jpn. J. Appl. Phys.* **27** (1988) L1476.
8. W. ZHU and P. S. NICHOLSON, *J. Mater. Res.* **7** (1992) 38.
9. T. SATA, K. SAKAI and S. TASHIRO, *J. Amer. Ceram. Soc.* **75** (1992) 805.
10. K. SATO, T. HIKATA, H. MUKAI, M. UEYAMA, T. KATO, T. MASUDA, M. NAGATA, K. IWATA and T. MITSUI, *IEEE. Trans. Magn.* **27** (1991) 1231.
11. Y. YAMADA, B. OBST and R. FLUKIGER, *Supercond. Sci. Technol.* **4** (1991) 165.
12. D. SHI, S. SALEM-SUGUI, Z. WANG, L. F. GOODRICH, S. X. DOU, H. K. LIU, Y. C. GUO and C. C. SORRELL, *Appl. Phys. Lett.* **59** (1991) 3171.
13. K. SATO, N. SHIBUTA, H. MUKAI, T. HIKATA, M. UEYAMA and T. KATO, *J. Appl. Phys.* **70** (1991) 6464.
14. E. YANGISAWA, T. MOROMOTO, D. R. DIETRICH, H. KUMAKURA, K. TOGANO and H. MAEDA, *Appl. Phys. Lett.* **54** (1989) 2602.
15. M. MIMURA, H. KUMAKURA, K. TOGANO and H. MAEDA, *ibid.* **54** (1989) 1582.
16. S. JIN, R. C. SHERWOOD, T. H. TIEFEL, G. W. KAMMLOTT, R. A. FASTNACHT, M. E. DAVIS and S. M. ZAHURAK, *ibid.* **52** (1988) 1628.
17. S. X. DOU, K. H. SONG, H. K. LIU, C. C. SORRELL, M. H. APPERLEY, A. J. GOUCH, N. SAVVIDES and D. W. HENSLEY, *Physica C* **160** (1989) 533.
18. Y. HWU, L. LOZZI, S. LA ROSA, M. MARSI, M. ONELLION, H. BERGER, F. FOGGO, F. LEVY and G. MARGARITONDO, *Solid State Commun.* **80** (1991) 701.
19. P. A. P. LINDBERG, Z. H. SHEN, I. LINDAU, W. E. SPICER, C. B. EOM and T. H. GEBALLE, *Appl. Phys. Lett.* **53** (1988) 529.
20. Y. FENG, D. C. LARBALISTIER, S. E. BABCOCK and J. B. VANDERSANDE, *ibid.* **61** (1992) 1234.
21. R. H. ARENDT, M. F. GARBAUSKS, E. L. HALL, K. W. LAY and J. E. TKACZYK, *Physica C* **194** (1992) 393.
22. D. BHATTACHARYA, L. C. PATHAK, S. K. MISHRA, D. SEN and K. L. CHOPRA, *Appl. Phys. Lett*. **57** (1990) 2145.
23. E. GEBHARDT and W. OBROWSKI, *Z. Metallik* **45** (1954) 33.
24. E. J. KOHLMEYER and H. HENNING, *Z. Erzbergbau Metallhuettenw* **7** (1954) 331.
25. D. E. MORRIS, C. T. HULTGREN, A. M. MARKELZ, J. Y. WEI, N. G. ASMAR and J. H. NICKEL, *Phys. Rev. B* **39** (1989) 6612.
26. Y. FENG, S. DANYLUK, K. C. GORETTA, N. CHEN, M. RUNDE, S. J. ROTHMAN and J. L. ROUTBORT, *Appl. Phys. Lett*. **60** (1992) 2291.
27. T. HATANO, K. AOTA, S. IKEDA, K. NAKAMURA and K. OGAWA, *Jpn. J. Appl. Phys*. **27** (1988) L2055.

Received 28 August 1997
and accepted 7 October 1998