

Preparation and characterization of silver clad (Bi, Pb)–Sr–Ca–Cu–O 2223 superconducting tapes with high critical current density

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Abstract. Silver clad Bi-2223 tapes with consistently high critical current densities of over 30,000 A/cm² at 77 K and zero field were prepared by powder-in-tube (PIT) technique. Powder XRD, electron microscopy, a.c. susceptibility and critical current measurements were used to study the phase assemblage, microstructure and transport properties of these tapes at various stages of processing. The precursor powder for PIT process was prepared by a sol-gel route by acrylate method using freshly prepared nitrates of Bi, Pb, Sr, Ca and Cu. The carbon content in the powder was minimized by subjecting it under dynamic vacuum calcination followed by heating in free flow of oxygen for long durations with intermittent grindings. The choice of initial stoichiometry, high reactivity of the precursor, effective removal of carbon, choice of phase assemblage at the filling stage and the multistage thermomechanical processing at optimized conditions were found to be responsible for the high critical current density.

Keywords. High T_c superconductor; tapes; Bi-2223; PIT process; critical current density.

1. Introduction

Among the several families of high T_c ceramic superconductors, (Bi, Pb)–Sr–Ca–Cu–O system has attracted the greatest attention for fabrication of superconducting wires and tapes. Three superconducting phases such as Bi-2201 ($T_c \approx 15$ K), Bi-2212 ($T_c \approx 90$ K) and Bi-2223 ($T_c \approx 110$ K) have been identified in the system. The 2223 phase offers a large temperature window for 77 K operation and shows very high J_c values at 77 K and irreversibility of fields below 30 K (Sato *et al* 1993) and possesses $H_{c2} > 41$ T (Kamakura *et al* 1990). Considerable effort has been made by various groups during the last few years to fabricate superconducting tapes with Bi-2223 phase by several techniques such as powder-in-tube (PIT) (Heine *et al* 1989; Nomura *et al* 1993; Damodaran *et al* 1994; Wang *et al* 1995), doctor-blade casting (Kase *et al* 1990, 1991), electrophoretic deposition (Ming *et al* 1994; Sun-li *et al* 1995) and dip coating (Shimoyama *et al* 1992) using powders synthesized by different routes. The PIT method has assumed greater significance because of the superior performance of the processed tapes particularly with respect to the transport properties and the ease of fabrication into long flexible tapes. Such tapes are being produced with consistently high critical current values of around 20,000 A/cm² at 77 K and zero field for short lengths.

In this paper we describe the results of our studies on preparation of short length Bi-2223 tapes by PIT technique using a highly reactive precursor powder synthesized by sol-gel route. The studies mainly include the choice of stoichiometry, standardization of

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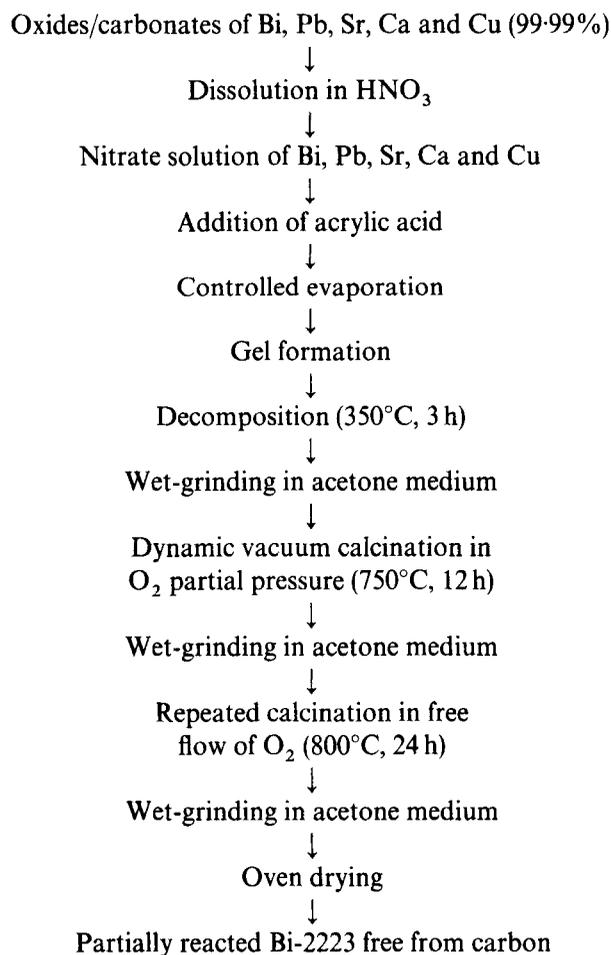
powder synthesis, process for carbon removal, optimization of thermo-mechanical properties and characterization of powder and tapes at different stages of processing by XRD, SEM, a.c. susceptibility and transport critical current density measurements.

2. Experimental

2.1 Powder synthesis

The composition of the starting powder was chosen as $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{2.2}\text{Cu}_3\text{O}_y$, after conducting an extensive study on the effect of stoichiometric variation of individual cations on Bi-2223 phase formation and critical current density in sintered pellets; the details of which are reported in one of our earlier publications (Simon *et al* 1994).

Flowsheet for preparation of bismuth-based oxide superconductor powder free from carbon



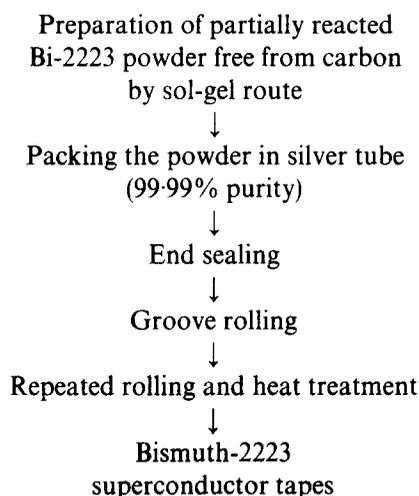
Flowsheet 1.

Superconducting powder for the PIT process was prepared by sol-gel method by acrylate route. In order to maintain the correct stoichiometry, high purity (99.99%) oxides/carbonates of Bi, Pb, Sr, Ca and Cu were dissolved in minimum amount of HNO_3 (1:1) to form their nitrates. The sol was prepared by adding requisite amount of acrylic acid. The solution was concentrated by heating at 100°C till a green gel was formed. It was then decomposed by heating at 350°C for 3 h. The powder obtained was wet-ground in acetone medium and dried. It was then subjected to dynamic vacuum calcination at 750°C for 12 h in reduced oxygen partial pressure. The powder was again wet-ground, and heated at 800°C for 24 h in free flow of oxygen with one intermediate grinding. It was once again wet-ground, oven dried and used as the precursor for tape fabrication. The process not only yielded highly reactive superconductor powder rich in 2212 phase but also eliminated carbon to a great extent. The schedule for synthesis of the precursor powder is given in flowsheet 1.

2.2 Tape fabrication and heat treatment

Ag clad tapes were fabricated by PIT technique. Ag was used as the sheath material because of its low reactivity with the superconductor and its good electrical and mechanical properties. The precursor powder was packed into high purity (99.99%) seamless Ag tubes (OD, 10.0 mm, ID, 7.5 mm, length 5–6 cm) with a packing density of around 3 g/cc. The ends of the tubes were closed with suitable Ag plugs and sealed mechanically. They were then rolled through a series of grooves to a diameter of 1–1.5 mm with intermediate annealings. Tapes were prepared from these wires by intermittent rolling-cum-heat treatments (up to 5 stages) at temperatures in the range $830\text{--}840^\circ\text{C}$ for various durations ranging from 50 to 250 h. The heat treatments of all the samples were carried out in muffle furnaces in which the temperature was controlled to an accuracy and stability of $\pm 1^\circ\text{C}$ employing programmable temperature controllers. The final thickness of the tapes thus prepared were $90\text{--}100\ \mu\text{m}$. A flowsheet for preparation of the tapes is given in flowsheet 2.

Flowsheet for preparation of Ag clad Bi-2223 tapes by PIT process



Flowsheet 2.

2.3 Characterization

The crystallinity and the sequence of phase evolution of the precursor powder as well as the tapes were studied by an automated X-ray diffractometer (Phillips PW 1710) using Cu K α radiation. The tape specimens for XRD were prepared by peeling off the Ag sheath followed by mild grinding and XRD patterns were taken using a specially made sample holder for analysing very small quantities of the sample. In some cases 'banana peeled' samples were directly used to study the surface characteristics of the superconductor core. The relative amounts of different phases were estimated by measuring the integrated intensities of the major XRD peaks of the corresponding phases such as 2223 ($2\theta = 34.1$), 2212 ($2\theta = 27.5$), 2201 ($2\theta = 29.8$), Ca_2PbO_4 ($2\theta = 17.6$) and CuO ($2\theta = 38.8$).

The microstructure of the heat treated tapes was studied by scanning electron microscopy (Hittachi S2400). Peeled samples were used to observe both the longitudinal and transverse view of the superconductor core employing back scattered electrons. A.c. susceptibility measurements as a function of temperature were conducted by employing a dual phase lock-in-amplifier (EG&G PAR 5210) and APD cryostat. The built-in oscillator of the lock-in-amplifier excited the primary coil at a frequency of 28.4 Hz and the signals from the secondary coil were detected. All measurements were carried out during the warming-up cycle at a very slow rate of 1°C/min to avoid thermal hysteric effects. J_c measurements were performed by conventional four-probe d.c. method at liquid nitrogen temperature using 1 $\mu\text{V}/\text{cm}$ criterion. A constant current source having a capacity of 30 A supplied the desired current and a nanovoltmeter (Keithley 181) was used to

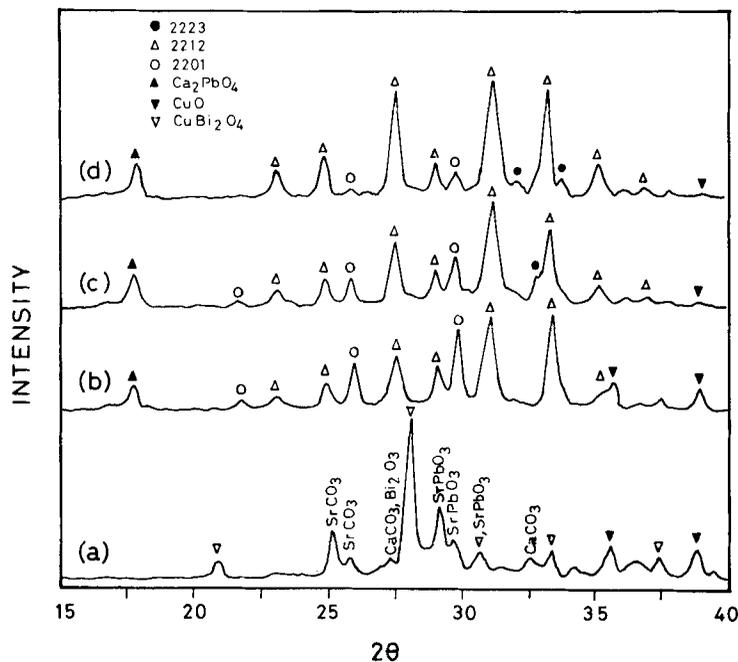


Figure 1. Evolution of XRD spectra at different stages of powder preparation: (a) powder obtained after the decomposition of the gel at 350°C, (b) vacuum calcined powder at 750°C for 12 h, (c) and (d) after subsequent heat treatments at 800°C for 12 h and 24 h, respectively in free flow of oxygen.

measure the voltage. All instruments for the above measurements were interfaced through a PC and the data collection was performed using appropriate softwares.

3. Results and discussion

It may be mentioned that one of the critical factors which determines the final tape performance is the choice of phase assemblage of the precursor powder for the PIT process. The initial studies conducted by the authors showed that powders rich in 2223 phase when used at the filling stage did not lead to tapes with high J_c values whereas precursors having high percentage of 2212 phase resulted in tapes with good transport properties. The reason (discussed in detail in the succeeding part) may be because of the reaction involving liquid phase of Ca_2PbO_4 and Ca^{2+} and Cu^{2+} ions for conversion of 2212 phase to 2223 phase which not only helps to heal the cracks produced during the intermittent rolling operation but also densify the superconductor core effectively during heat treatment. This subsequently reduces the weak links and improves the J_c . Therefore, in the present investigation, the conditions for the precursor powder preparation has been set such that the process yields powder having maximum 2212 phase.

Figure 1 shows the evolution of XRD spectra at different stages of powder preparation. The diffraction data shows that the powder obtained by the decomposition of the gel at 350°C (figure 1a) is crystalline and comprises CuBi_2O_4 , SrPbO_3 , SrCO_3 , CaCO_3 , CuO , Bi_2O_3 and traces of some unidentified phases. The dynamic vacuum calcination in reduced oxygen partial pressure (5 torr, oxygen flow rate – 3 l/min) at 750°C for 12 h is

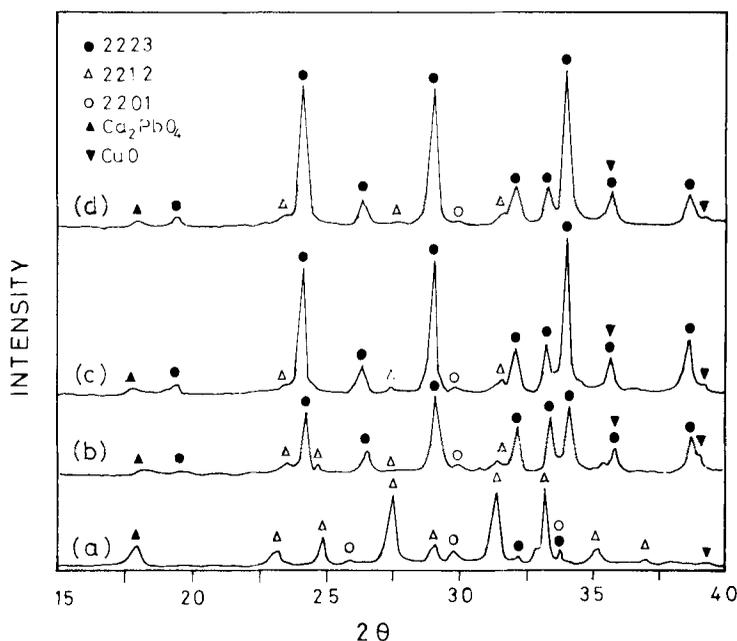


Figure 2. Sequence of phase changes in the superconductor core of the tape specimens during a three-stage rolling-cum-heat treatment schedule: (a) precursor, (b) 100 h, (c) 200 h and (d) 250 h.

found to be very effective in converting the above reactants into mainly 2212, 2201 and Ca_2PbO_4 phases (figure 1b). Figure 1 (c and d) shows that subsequent heat treatments of the powder at 800°C for 24 h in two stages enrich the 2212 phase with decrease in 2201 and Ca_2PbO_4 phases. The volume fraction of different phases in the precursor powder as estimated from the XRD pattern (figure 1d) is 2212, 67.3%; 2201, 12.1%; Ca_2PbO_4 , 18.6% and 2223, 2%.

Figure 2 shows the sequence of phase changes in the superconductor core of the tape specimens during a three-stage rolling-cum-heat treatment schedule i.e. 100 + 100 + 50 h at $830\text{--}840^\circ\text{C}$. The XRD pattern for the precursor powder is also included in the figure for comparison. The volume percentage of individual phases during each stage of heat treatment is given in table 1. It is seen that after 100 h of heat treatment the volume fraction of 2223 phase reaches 73.3%. Significant quantities of 2212 (8.9%), Ca_2PbO_4 (8.2%) and CuO (6.6%) phases are also detected together with minor quantity of 2201 (3.0%) phase. Further heat treatment of the tapes for the next 100 h increases the 2223 phase to 85.9% with reduction of both 2212 (4.0%) and Ca_2PbO_4 (4.2%) phases. After 250 h the 2223 phase fraction attains a value of 89.1% with very low contents of 2212 (1.6%) and 2201 (1.5%) phases along with Ca_2PbO_4 (3.9%) and CuO (3.9%) phases. Subsequent heat treatments beyond 250 h did not show any significant change in the phase assemblage.

Figure 3 shows a comparison of XRD patterns obtained on the surface of the peeled tape's core and the ground powder of the core. It is quite evident that the (00l) peaks of the diffraction pattern of the tape's surface (figure 3a) have a sharp increase in intensities showing increased texturing of the tape's surface along the rolling direction i.e. along the a-b plane. Further, it is interesting to note that the impurity phases such as 2212, Ca_2PbO_4 , 2201 and CuO are remarkably less on the surface compared to the interior. Table 2 gives a comparison of XRD intensities of different phases on the surface and interior of the core under identical conditions. It is seen that on the core surface 2212 and 2201 phases are undetectable and Ca_2PbO_4 and CuO counts are significantly less compared to the interior.

Figure 4 shows the SEM back scattered micrographs of both transverse and longitudinal sections of the tape core at various stages of rolling cum heat treatment schedule. In all cases the micrographs were taken on fractured surfaces. The micrograph of the vertical section of the sample which had undergone 3 stages of rolling and 250 h of heat treatment (figure 1a) shows that the interlocked Bi-2223 platelets are densely packed and uniformly reacted. Microstructures of the longitudinal sections (figures 4 b–d) show the enhancement of Bi-2223 grain orientation along the rolling direction after each stage of rolling cum heat treatment. Figure 1e shows an enlarged view of Bi-2223 grains oriented along the rolling direction after three stages of rolling and 250 h of heat treatment. It is evident from the microstructures of the longitudinal sections that the grains which were randomly

Table 1. Volume percentage of individual phases during each stage of heat treatment of the tapes.

Duration	2223	2212	2201	Ca_2PbO_4	CuO
100 h	73.3	8.9	3.0	8.2	6.6
200 h	85.9	4.0	4.4	4.2	5.5
250 h	89.1	1.6	1.5	3.9	3.9

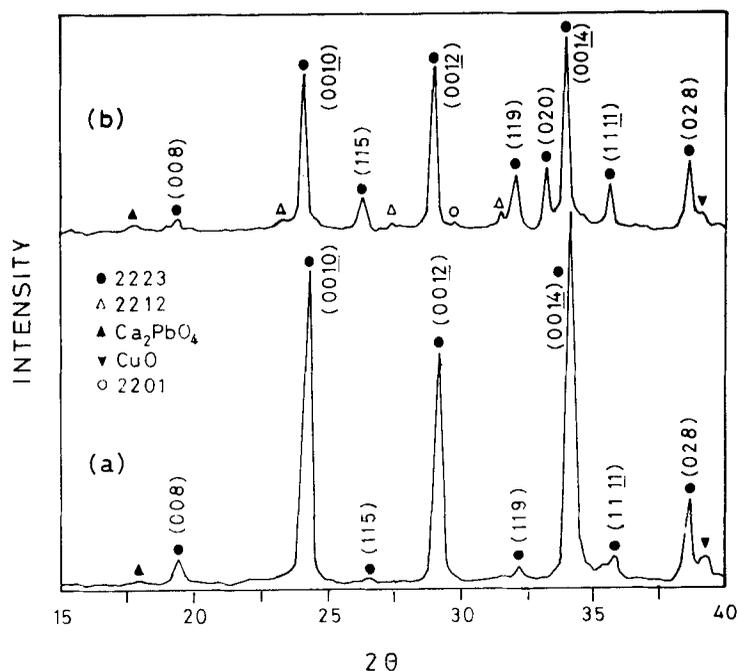


Figure 3. Comparison of XRD patterns taken on the surface (a) and interior (b) of the superconductor core. The surface shows increased texturing and lesser secondary phases.

Table 2. Comparison of XRD peak intensities on the surface and interior of the superconducting core after three stages of rolling and 250 h of heat treatment.

Sample	2223	2212	2201	Ca ₂ PbO ₄	CuO
Surface	2673	ND	ND	29	39
Interior	1431	27	26	62	63

ND, Not detected

oriented during the initial stages of rolling cum heat treatment have progressively aligned in each subsequent stages and have attained a high degree of orientation and good intergrain connectivity after the final stage.

Figure 5 shows the a.c. susceptibility vs temperature (χ' - T) plots for the precursor powder (a) and tape samples heat treated for 100 h (b) and 250 h (c). As can be seen from figure 5a, the precursor powder undergoes a diffused superconducting transition with T_c around 80 K showing that the major phase content is 2212. The diffused phase transition is indicative of weak links associated with powder sample. χ' - T plot for tape sample heat treated for 100 h (figure 5b) shows two distinctive superconducting transitions; one at 110 K corresponding to Bi-2223 phase and the other at 104 K. The second transition occurring intermediate between the transition temperatures of 2223 and 2212 phases is

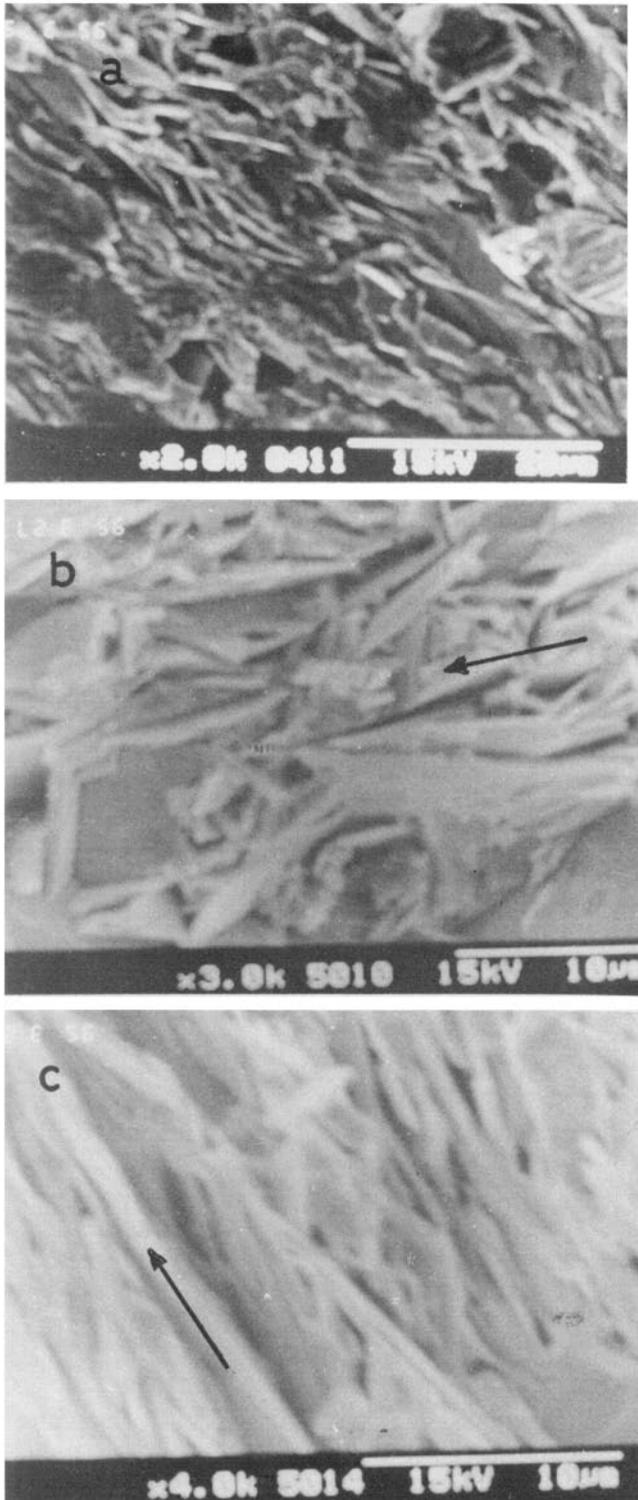


Figure 4. a-c.

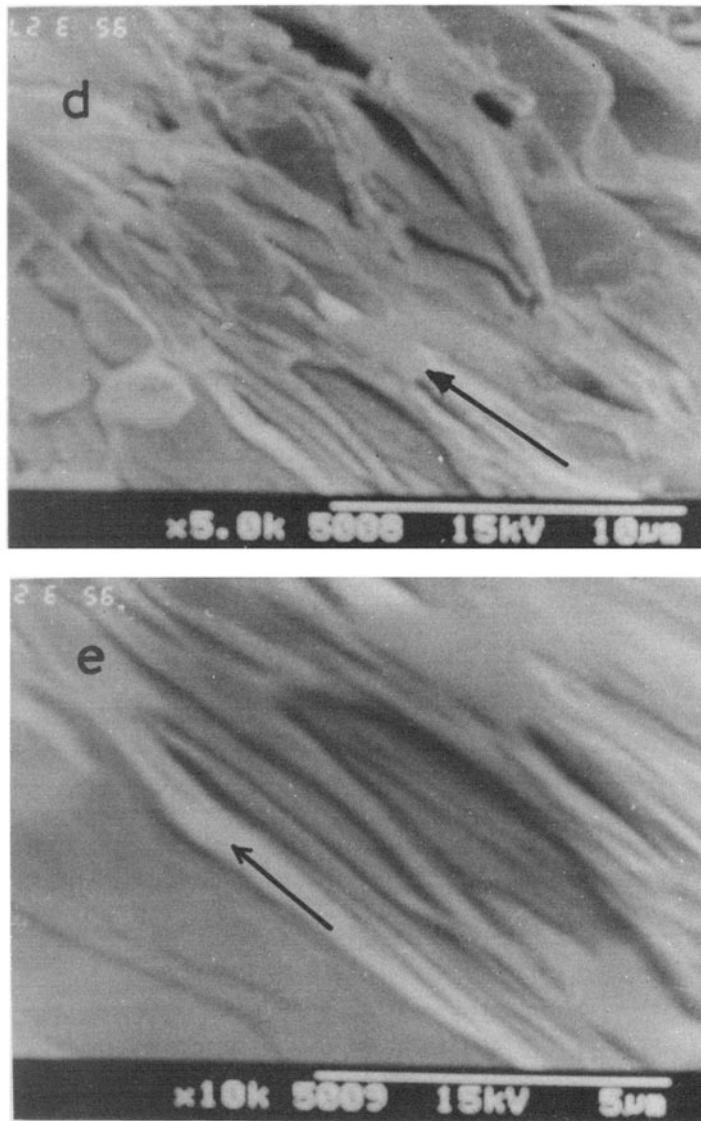


Figure 4. SEM back scattered micrographs of transverse and longitudinal sections of the tape-core: (a) transverse section showing interlocked Bi-2223 platelets, (b–d) longitudinal sections showing enhancement of Bi-2223 grain orientation along the rolling direction after each stage of rolling cum heat treatment and (e) enlarged view of oriented Bi-2223 grains after the final stage. Rolling direction is indicated by arrow mark.

due to the intergrowth of the above structurally identical phases and the presence of weak links. Figure 5c shows $\chi-T$ plots for the tape sample heat treated for 250 h and had undergone 3 intermediate rollings. The plot shows a sharp transition at 110 K with no sign of any double transition indicating the absence of intergrowths and weak links.

Figure 6 shows the voltage vs critical current density ($E-J$) plots for two typical tape samples which had undergone cumulative 200 h and 250 h of heat treatments in which the

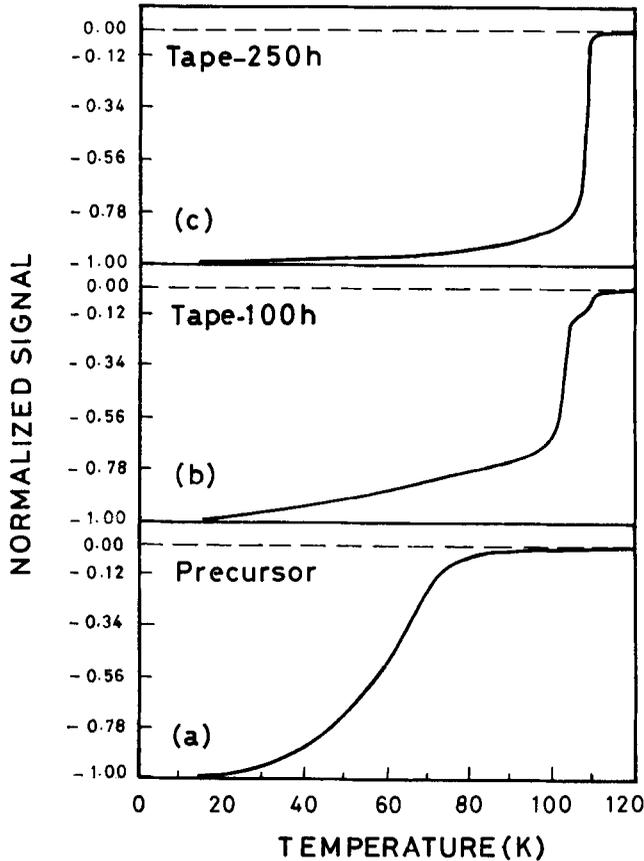


Figure 5. A.c. susceptibility vs temperature plots: (a) precursor powder, (b) tape heat treated for 100 h and (c) tape heat treated for 250 h.

voltage measurements were carried out over a length of 1 cm of the sample. Considering the $1 \mu\text{V}/\text{cm}$ criterion, the transport critical current values obtained are $24,500 \text{ A}/\text{cm}^2$ and $31,500 \text{ A}/\text{cm}^2$ at 77 K and self field for the tapes heat treated for 200 h and 250 h respectively. The values were reproducible within 10% for a number of samples chosen from the same batch as well as from different batches.

The important factors which determine the transport properties of Ag clad Bi-2223 tapes are: (i) phase purity of the superconductor core, (ii) grain alignment and (iii) core density.

There are a number of constraints in fabricating phase pure Bi-2223. The system contains as many as 5 cations with dissimilar mobility and reactivity. As a result two or more of the ingredients can react together and form several impurity phases. In addition, the stability of Bi-2223 phase is limited within a very narrow temperature range depending on the starting composition and it always lies close to the melting point (Yang Lin Chen and Ronald Stevens 1992a). Further, 2223 phase is structurally similar to 2212 and 2201 phases, which often results in an intergrowth of these phases. Many other difficulties arise in case of tape fabrication in which it is necessary to form the 2223 phase *in situ*. The difficulties are mainly the inaccessibility of the powder for intermediate processing (such

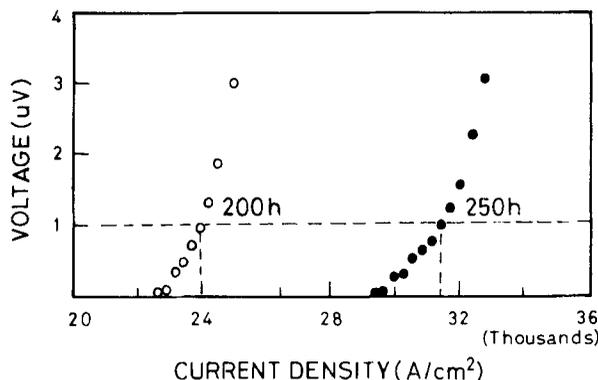


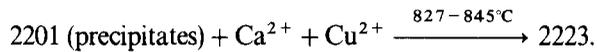
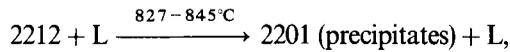
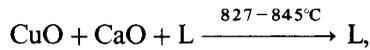
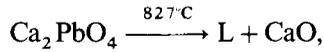
Figure 6. Voltage vs critical current density (E - J) plots.

as grinding) and limitation of pressure that can be applied during the rolling operation. Process conditions such as initial stoichiometry, method of powder synthesis, temperature, atmosphere, heating and cooling rates, duration of heat treatment, number of stages of thermomechanical treatments etc are found to have direct influence on the formation of 2223 phase and therefore a judicious choice of the above parameters are vital in order to achieve maximum 2223 phase in the processed tapes.

The sequence of reactions that takes place during the different stages of synthesis of the precursor and heat treatment of the tapes can be explained with reference to the XRD results as follows. Among the isostructural phases of Bi-system 2201 phase is found to have the largest negative free energy of formation and hence formation of this phase starts at relatively lower temperatures ($\sim 700^\circ\text{C}$) than those required for 2212 ($\sim 827^\circ\text{C}$) and 2223 ($\sim 845^\circ\text{C}$) phases. It is also known that PbO added to the system reacts with CaCO_3 at temperatures as low as 680°C to form Ca_2PbO_4 . XRD data for the vacuum calcined powder at 750°C (figure 1) shows presence of significant quantities of 2212 phase in addition to 2201 and Ca_2PbO_4 phases which indicates the high reactivity of the sol-gel synthesized powder. As the temperature for the next heat treatment is increased to 800°C which is close to the phase stability region of 2212 phase significant quantities of 2201 phase converts into 2212 phase as seen from figure 1. It may be emphasized here that by the above process it has been possible to synthesize precursor powder rich in 2212 phase at a lower temperature than that used in a conventional solid state route. Therefore the above process yielded fine grained and highly reactive precursor powder for the PIT process. Further, the carbon content in the powder at the filling stage is a limiting factor for the transport properties of the tapes. Carbon segregates at the grain boundaries causing poor connectivity between the grains (Zhang and Hellstrom 1992). Hence it is very important to find out proper methods to synthesize carbon-free powders for fabrication of superconducting tapes by PIT process. The incorporation of dynamic vacuum calcination under reduced oxygen partial pressure followed by heat treatment for long durations (24 h) in free flow of oxygen with intermittent grindings helps to minimize the carbon content in the precursor powder.

The heat treatment of the tapes in the present work was carried out at a temperature in the range 830 – 840°C which was 10 – 12°C lower than the temperature optimized for sintering Bi-2223 pellets. The reaction sequences within the tapes during the heat treatment can be understood in the light of the model proposed by Yang Ling Chen *et al*

(1992b) in conjunction with the XRD results. At 827°C Ca_2PbO_4 available in the precursor decomposes to form a liquid phase and CaO. The CaO thus formed together with CuO available in the precursor dissolves into the liquid phase. The liquid phase so formed containing mainly Ca^{2+} , Cu^{2+} and Pb^{2+} reacts with 2212 phase resulting in the precipitation of 2201 and subsequent nucleation of 2223 phase through the reaction between 2201 and Ca^{2+} and Cu^{2+} ions from the liquid phase as shown below.



It is seen from table 1 that the volume fraction of Ca_2PbO_4 , 2212, 2201 and CuO phases monotonically decreases after each stage of heat treatment of the tapes with a corresponding increase in 2223 phase. The volume percentage of 2223 phase after the final treatment stage (250 h) is 89.1%.

Mechanical processing plays a key role in the fabrication of Bi-based superconducting tapes. Bi-based compounds have highly anisotropic electrical and magnetic properties. It is reported (Martin *et al* 1988) that the resistance R_c along the c-axis is 10^5 times larger than R_a , that along a-axis and R_a/R_b varies from 1.5 to 2. It is therefore essential to align the material in such a way that the a-b plane is parallel to the direction of current flow. If the mechanical processing, i.e. rolling, is strictly optimized and performed repeatedly after each heat treatment stage, it can not only align the platelet-like 2223 grains along the rolling direction (a-b plane) but also compact and densify the superconductor core effectively. During the rolling process the metal sheath work hardens and helps to retain the compaction. After an intermediate heat treatment the sheath becomes soft while the core gets sintered and densify further. Mechanical processing also enhances the formation of Bi-2223 phase by breaking up of the reactant phases and bringing them into better contact with one another. The microstructures shown in figure 4 shows that the thermo-mechanical schedule employed in the present investigation has effectively aligned the platelet like grains of Bi-2223 along the rolling direction with good intergrain connectivity.

XRD analysis of the surface and interior of the superconductor core (figure 3) reveals that the surface has better texture and lesser secondary phases compared to the interior. It is therefore expected that by further improving the mechanical processing together with a better knowledge of the kinetics it may be possible to fabricate Bi-2223 tapes with J_c values close to the highest values achieved in the surface.

4. Conclusions

- (i) It has been possible to fabricate Ag clad Bi-2223 superconducting tapes by PIT process with J_c values over 30,000 A/cm² with good consistency.

- (ii) The sequence of phase evolution, microstructure and electro-magnetic properties of the tapes during the different stages of processing has been studied by XRD, SEM, a.c. susceptibility and J_c measurements.
- (iii) The important factors which have contributed to the high J_c are: (a) maintenance of desired stoichiometry, (b) high reactivity of the precursor, (c) effective removal of carbon, (d) choice of phase assemblage at the filling stage and (e) multistage thermo-mechanical processing at optimized conditions.
- (iv) The grain alignment and phase purity of Bi-2223 phase at the surface of the superconductor core are found to be remarkably higher than the interior of the core. This implies that the surface will have a much higher J_c than the core. Hence there is a great scope for further improving the overall J_c by improved mechanical processing together with a better knowledge of the kinetics.

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