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Critical current in Ag/BPSCCO tapes using low purity materials

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Abstract. Silver-clad $Bi_{1\cdot7}Pb_{0\cdot4}Sr_{1\cdot8}Ca_2Cu_{3\cdot5}O_x$ (BPSCCO) tapes have been fabricated using low purity (98–99%) starting materials and following the powder-in-tube technique. Maximum J_c values of $6\cdot14 \times 10^3\,A\cdot cm^{-2}$ at 77 K and $1\cdot4 \times 10^5\,A\cdot cm^{-2}$ at 4·2 K have been obtained in tapes subjected to the process of intermediate rolling and sintering. The bulk superconducting material used for the tape-fabrication contains both 2223 and 2212 phases in the ratio 60:40. A pure phase material and the optimization of the sintering parameters are expected to yield much higher J_c values at 77 K. It is possible that the copper-rich phase(s) and/or a small amount of iron impurity (60 ppm) present in CuO might be acting as flux pinning sites and could be responsible for high J_c values.

Keywords. Critical current density; tapes; BPSCCO system; sintering; flux pinning; powder-in-tube technique.

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1. Introduction

At present, the Bi–Sr–Ca–Cu–O (BSCCO) superconductor (Maeda *et al* 1988) appears to be the best choice for developing metal-clad high T_c wires/tapes for magnet-based applications which can be operated at 77 K. The factors which favour the development of the BSCCO wires and tapes are the following:

1. The composition $Bi_2Sr_2Ca_2Cu_3O_x$, the so-called 2223 phase has a T_c of 110 K, well above 77 K.
2. Its sintering temperature (~ 850°C) is well below the melting point of silver, used as a cladding material (compared with the sintering temperature ~ 930°C required for Y–Ba–Cu–O (YBCO).
3. The BSCCO superconductor is formed in air or reduced oxygen pressure and is not as sensitive to O-stoichiometry as the YBCO. Ideal oxygen stoichiometry is easier to obtain in Ag/BSCCO wires/tapes.
4. BSCCO is not toxic like Tl–Ba–Ca–Cu–O. (TBCCO) which otherwise has a T_c of 120 K.

The 2223 phase of the BSCCO system is not readily obtained in pure form but is stabilized with the partial substitution of bismuth by lead (Takano *et al* 1988). Further, a practical superconductor is characterized by the high values of the critical parameters viz., T_c, H_{c2} and J_c. This system does have high T_c(110 K) and high $H_{c2} \sim 41$ T (Kumakura *et al* 1988) but the transport (intergrain) critical current is restricted by the intergrain weak links, a common feature of all the oxide superconductors. BSCCO also has large anisotropies of J_c and H_{c2}, their values being much higher in the *a–b* plane compared to those along the *c*-axis. Attempts have therefore been made to obtain high J_c values by reducing the grain boundaries separation and obtaining good alignment of the grains.

Further, it is well-known that the J_c value of a pure and homogeneous superconductor drops rather sharply with magnetic field (current induced self field as well as applied field) as flux lines start moving under the influence of the Lorentz force. The flux lines can, however, be held back by the introduction of inhomogeneities such as lattice defects, grain boundaries and fine precipitates etc. in the material thus making them, the so-called 'dirty' superconductors. These inhomogeneities act as flux pinning sites and prevent flux line movement until a large J_c is reached. Fine nonsuperconducting phases, such as $CaSrPbO_4$, $Sr_2Ca_2Cu_3O_x$ and Ca_2CuO_3 have indeed been reported(Hikata *et al* 1989) to be acting as flux pinning sites in Ag-sheathed BPSCCO tapes having excess copper in the core material. A J_c value of 17400 A·cm^{-2} (77 K, 0 T) has thus been reported for the tapes by these authors. It thus appears that perhaps one can use low purity commerical grade ingredients wherein the impurities present might provide flux pinning sites and lead to high J_c values. Besides being advantageous in increasing J_c, the use of low purity oxides, carbonates etc. will bring down the cost of production of these tapes significantly. Low cost is a crucial criterion for any large scale production technology that has to be economically viable. In this communication we report our results on J_c of the Ag/BPSCCO tapes using commercial grade (locally available) material and fabricated by the powder-in-tube method. An excess Cu-cation ratio has been used in the preparation of superconducting material and a repeat rolling and sintering has been carried out during the processing of the tapes.

2. Experimental

Appropriate quantities of Bi_2O_3 (99%), PbO (98%), $Sr(NO_3)_2$ (99%), $CaCO_3$ (99%) and CuO (99%) as per the composition $Bi_{1\cdot6}Pb_{0\cdot5}Sr_{1\cdot8}Ca_2Cu_{3\cdot5}O_x$ were mixed and ground together. The mass was calcined in air at 810°C for 12 h. The second calcination was carried out after intermediate grinding at 840°C for 54 h. The material was crushed, ground, pelletized and sintered at 845°C for 70 h in air and furnace cooled. The pellets were ground to fine powder once again and packed in silver tubes (commercial grade marked '999') of O.D. 10 mm and I.D. 8 mm. The composite tube was rolled to wire of 1·5 mm × 1·5 mm cross section then to tapes of varying thicknesses with intermediate annealings as described earlier (Shukla *et al* 1991). These tapes, referred to as specimen Nos 40, 41 and 42 (first set) in table 1, were sintered in air at 845°C for 20 h. Part of these sintered tapes were rolled again and resintered at 845°C for 20 h. These tapes have been designated as specimen Nos 45, 46 and 48 (second set) in table 1. Critical current I_c was determined at 77 K and 4·2 K as per the 1 μV/cm criterion by the four-probe method. J_c values were then calculated after dividing I_c values by the area cross-section of the core. The grain structure was studied by obtaining SEM pictures on the fructured cross section of the tapes. Room temperature XRD spectra were obtained (using Cu–K_α radiation) on the bulk material as well as on the core material of the tape specimen nos 41 and 48 after removing silver sheath from one side.

Table 1. The sintering parameters, dimensions of the tapes and the cores along with the values of I_c and J_c of Ag/$Bi_{1·7}Pb_{0·4}Sr_{1·8}Ca_2Cu_{3·5}O_x$ tape specimens.

Set No.	Specimen No.	Sintering parameters	Tape-size t(mm) × w(mm)	Core-size t(mm) × w(mm)	I_c(A)		J_c(A·cm^{-2})	
					77(K)	4·2(K)	77(K) × 10^3	4·2(K) × 15^5
	40		0·74 × 1·39	0·22 × 0·68	0·33	11·6	0·22	0·077
First	41	845°C × 20 h	0·50 × 1·79	0·14 × 0·71	0·32	11·0	0·32	0·11
	42		0·24 × 2·08	0·009 × 0·89	0·30	10·5	3·75	1·31
	45	845°C × 20 h +	0·48 × 1·89	0·18 × 0·71	0·75	10·5	0·58	0·082
Second	46	Roll +	0·27 × 2·08	0·08 × 0·80	0·65	11·7	1·02	0·183
	48	845°C × 20 h	0·14 × 2·21	0·007 × 0·93	0·40	9·7	6·14*	1·49*

*Highest J_c values at 77 K and 4·2 K.

3. Results and discussion

Figures 1 and 2 show the I–V plots of all the tape specimens obtained experimentally at the 77 K and 4·2 K respectively. The calculated J_c values are indicated against each specimen in both the figures. The dimensions of the tapes and the cores alongwith I_c and J_c values are given in table 1. Two important features can be noted from table 1. The J_c of the tapes of both the sets increase with the reduction of the size of the tape (and the core) in conformity with the published data (for example Kawashima *et al* 1989) and our own recent studies (Shukla *et al* 1991). The second feature is that the J_c of the tape specimens of the second set are higher than the values for the tapes of the first set. The increase in J_c of the tapes of the second set is caused by the repeat rolling and sintering which is known (Togano *et al* 1989) to be an effective technique for improving the J_c of the 2223 phase through grain alignment.

The grain structure of the tapes of the two sets is shown in figures 3 and 4. It is clearly seen from these figures that the degree of grain alignment increases with the reduction of the tape thickness. The rolling of the tapes leads to an increased mechanical grain alignment. Thus the tape specimens 42 and 48 which have highest J_c values in the first set and the second set respectively also show the best grain alignment. Compared to the first set the tapes of the second set have a much denser layered grain structure. The intermediate rolling and sintering thus leads to a well-aligned grain structure and high J_c.

The bulk material used for the fabrication of the tapes has both 2223 and 2212 phases in the ratio 60:40 as determined by the intensity ratio of the (002) reflections of the two phases. The volume fraction of the 2223 phase does increase in tapes of the second set as seen from the XRD of the tape No. 48. Intermediate rolling and sintering causes this increase in the phase fraction of the 2223 phase. Tape specimens Nos 41 and 48 show very sharp (001) reflections very similar to that reported by us in a recent publication (Shukla *et al* 1991). This sharpness of the (001) reflections indicate a strong alignment of the grains along the *c*-axis.

Thus we find that high J_c values are possible in the Ag/BPSCCO tapes even with low purity starting materials. The variation of J_c with core thickness is shown in figure 5. It is interesting to note that at 77 K, the J_c of the tapes of the second set (with intermediate rolling and sintering) lie above the J_c values of the tapes of the

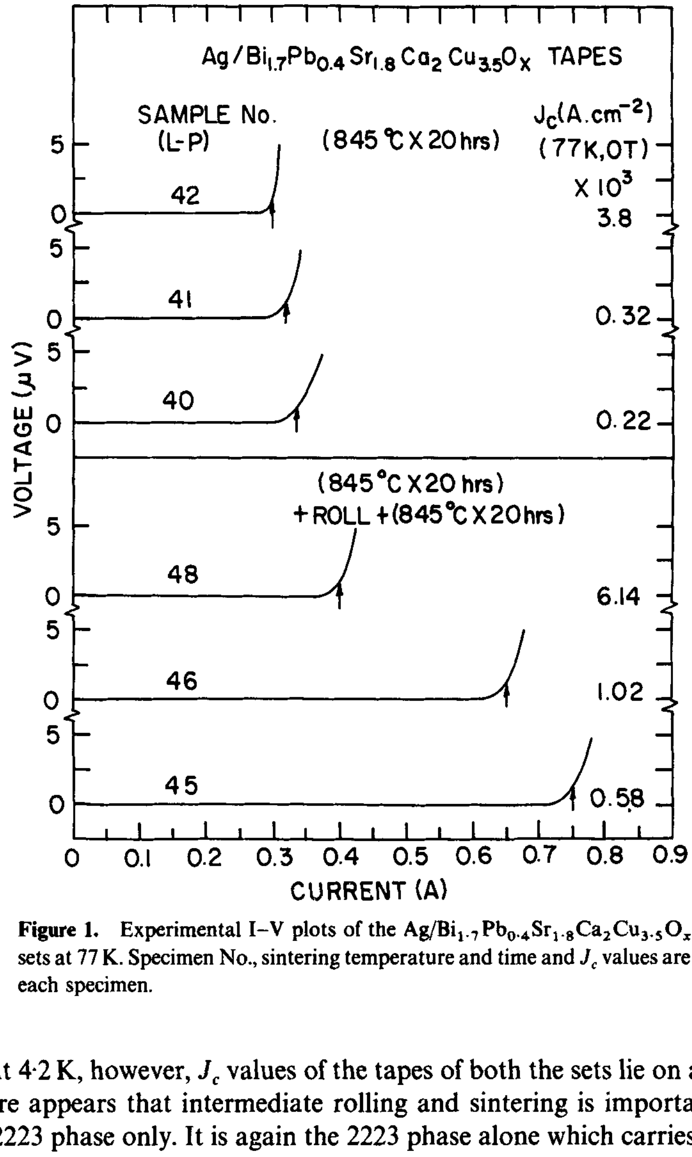

Figure 1. Experimental I–V plots of the $Ag/Bi_{1.7}Pb_{0.4}Sr_{1.8}Ca_2Cu_{3.5}O_x$ tapes of the two sets at 77 K. Specimen No., sintering temperature and time and J_c values are indicated against each specimen.

first set. At 4·2 K, however, J_c values of the tapes of both the sets lie on a single curve. It therefore appears that intermediate rolling and sintering is important for raising J_c of the 2223 phase only. It is again the 2223 phase alone which carries supercurrent at 77 K, the 2212 phase will hardly carry supercurrent as the T_c of this phase is too close to 77 K. At 4·2 K, on the other hand, the two phases are reported to have similar J_c values even in the presence of high magnetic field (Kumakura *et al* 1990). This is confirmed by our experimental data as the J_c values of the tape specimens of the first set and the second set at 4·2 K lie on a single curve. Larger fraction of 2223 phase is thus important at 77 K only and not at 4·2 K.

The highest J_c values obtained in the present studies viz., $6{\cdot}14 \times 10^3$ A·cm^{-2} (77 K) and $1{\cdot}49 \times 10^5$ A·cm^{-2} (4·2 K) are significantly higher than the best values of $J_c = 1{\cdot}85 \times 10^3$ A·cm^{-2} (77 K) and $2{\cdot}43 \times 10^4$ A·cm^{-2} (4·2 K) reported by us recently (Shukla *et al* 1991) for similarly processed tapes but using high purity (4N) materials. Two reasons are possible for this enhancement of J_c. One reason could be a better degree of grain alignment in these tapes and the other could be the presence of some impurity phases which might be acting as flux pinning sites. Unfortunately the quality

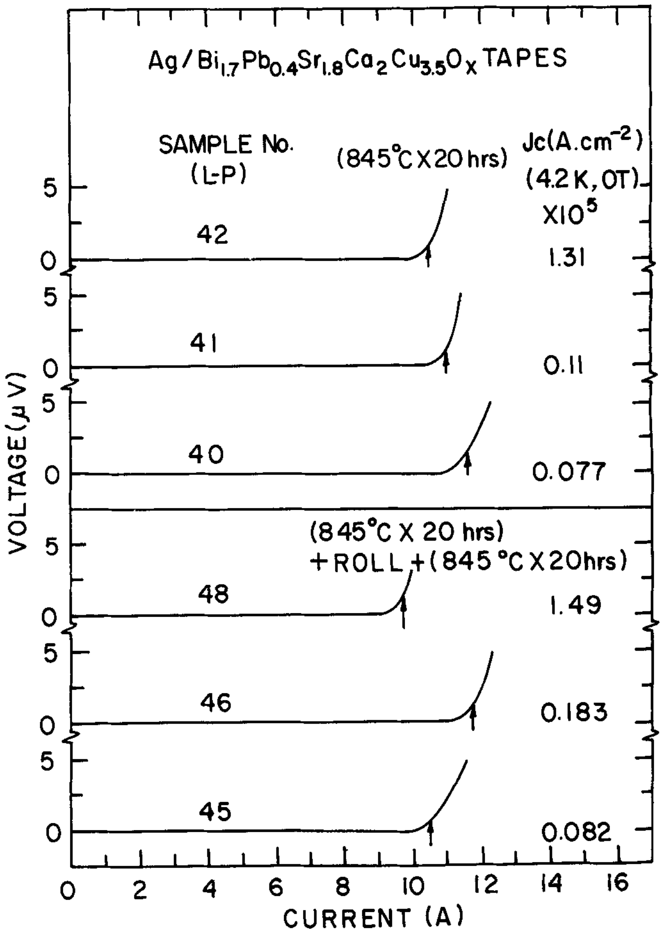

Figure 2. Experimental I–V plots of the Ag/$Bi_{1.7}Pb_{0.4}Sr_{1.8}Ca_2Cu_{3.5}O_x$ tapes of the two sets at 4·2 K. Specimen No., sintering temperature and time and J_c values are indicated against each specimen.

of the XRD spectra obtained on tape specimens Nos 41 and 48 was poor because of a very small quantity of the core material which could be exposed to X-ray after the removal of the silver sheath. A quantitative estimate of the degree of grain alignment could not therefore be made. The reduction of the core thickness achieved in the present studies (compare the core thicknesses of the specimens Nos 40 and 48) is 30 compared to maximum reduction of thickness by a factor of only 3 in the previous studies (specimens Nos 1 and 9 in Shukla *et al* 1991). This large reduction in the core thickness is certainly bound to increased grain alignment and enhanced J_c.

Our CuO material, as analysed by the atomic absorption spectroscopy, contains an impurity of 60 ppm iron. It will be interesting to know if iron, which is known to substitute at the Cu-site (Tang *et al* 1990) could provide flux pinning sites and enhance J_c. Large intragranular pinning forces have indeed been reported by Wordenweber *et al* (1989) in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ (for $x \lesssim 0{\cdot}01$) having an isostructural layered material. Mössbauer studies carried out on a variety of 2212 and 2223 BSCCO superconductors with the addition of 1·5% iron in place of copper (Tang *et al* 1990) show stacking faults and intergrowth of different phases on the microscopic level.

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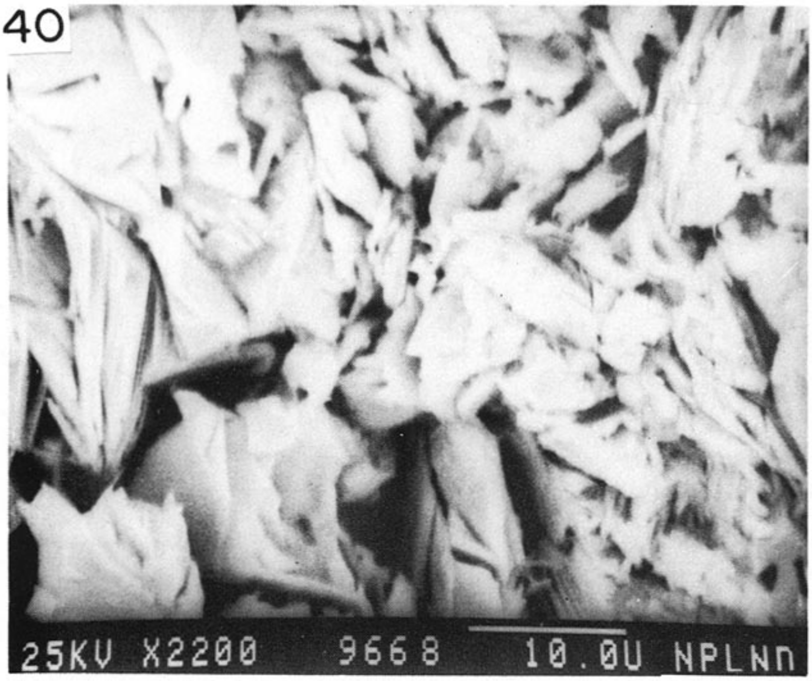

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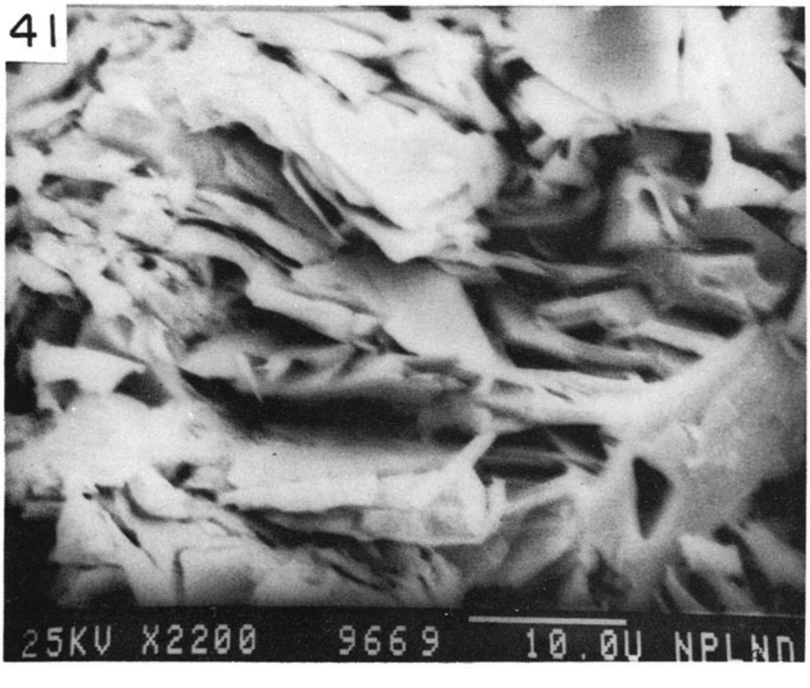


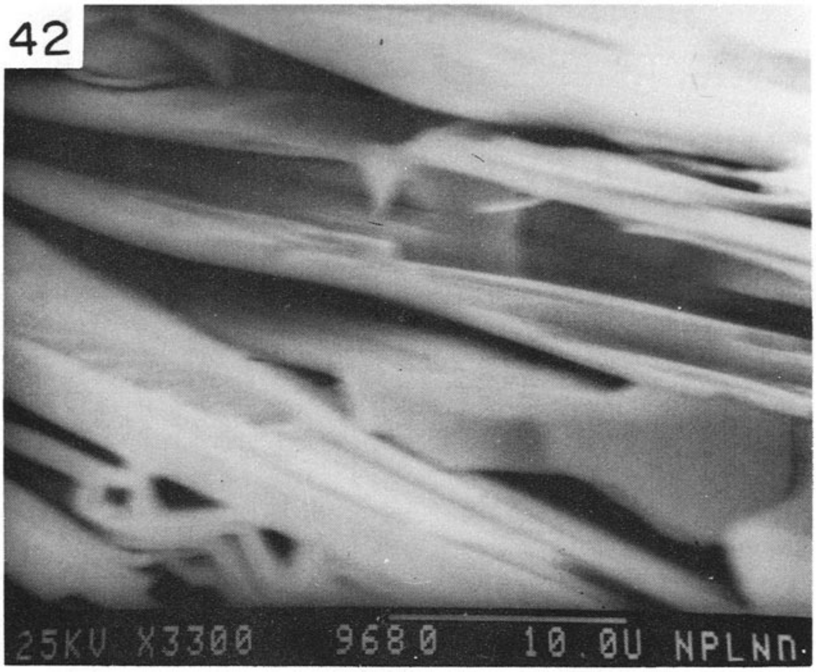
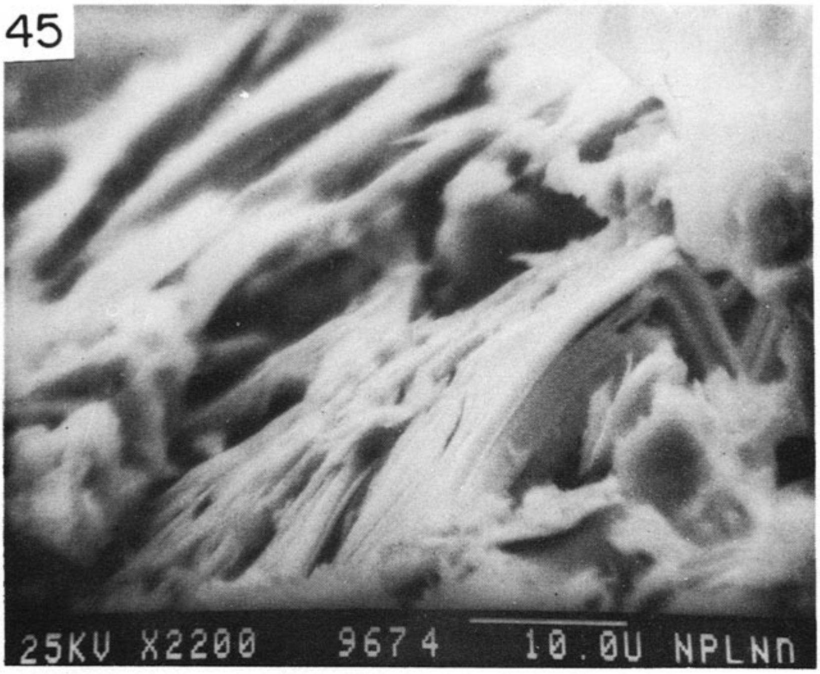


Figure 3. SEM micrographs of the fractured cross sections of the tape specimens Nos 40, 41 and 42 as detailed in table 1. Grain alignment improves from specimen No. 40 to specimen No. 42 as the core thickness is reduced.

Stacking faults and lattice distortions have been identified as the possible flux pinning sites in the BSCCO system by Shi *et al* (1989). These authors also report that copper and calcium-rich precipitates in this system introduced by the supersaturation of extra calcium and copper in the starting material by rapid solidification lead to enhanced J_c. Our BPSCCO material used for tape fabrication does have $Cu_{3\cdot 5}$ instead of the stoichiometric $Cu_{3\cdot 0}$. It is just possible that this excess copper precipitates out in the matrix as calcium and/or copper rich phases as discussed above and provide pinning sites.

To understand the possible role of the iron impurity and the excess copper in the bulk BPSCCO material it is essential to estimate the size of the defects through detailed lattice imaging studies. It is to be emphasized that the pinning sites in high T_c oxide superconductors are quite different from those effective in conventional superconductors. Since the pinning site has to be of the size of the coherence length ξ, which is only 10–20 Å, the pinning sites in the present materials thus has to be of the atomic lattice dimensions. Detailed studies of the lattice imaging on these tapes' core material are in progress to verify these possibilities. A whole new series of BPSCCO material with varying amount of iron addition and with different cation ratios are already under preparation. Further, since the starting bulk material used for the tape fabrication contains about 40% 2212 (low T_c phase), the J_c at 77 K is expected to increase substantially if the starting material is a pure 2223 phase. Attempts to synthesize single phase 2223 material using the same low purity oxides, carbonates and nitrates are presently on.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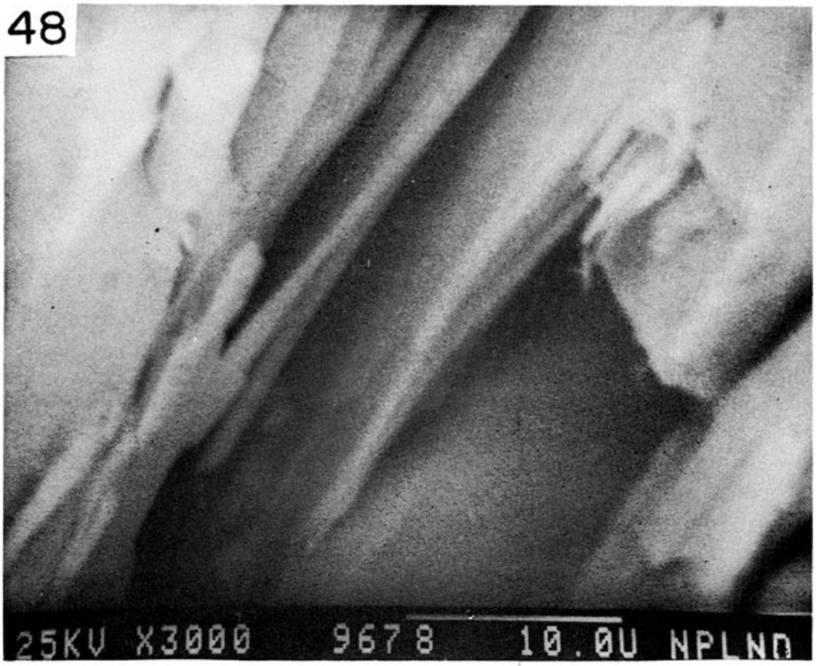

Figure 4. SEM micrographs of the fractured cross sections of the tape specimen Nos 45, 46 and 48 as detailed in table 1. Grain alignment improves from specimen No. 45 to specimen No. 48.

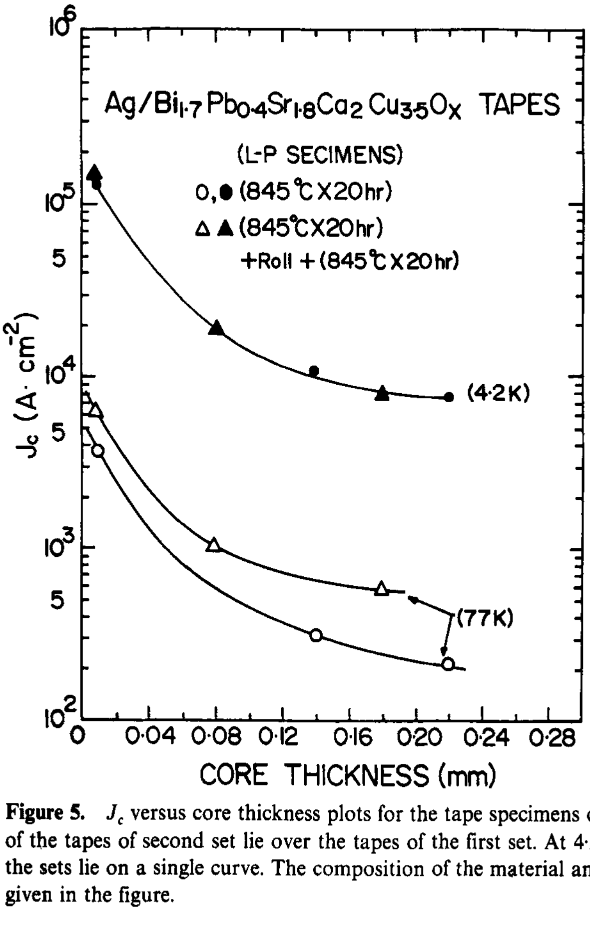

Figure 5. J_c versus core thickness plots for the tape specimens of both the sets. At 77 K J_c of the tapes of second set lie over the tapes of the first set. At 4·2 K J_c of the tapes of both the sets lie on a single curve. The composition of the material and sintering parameters are given in the figure.

4. Conclusions

We thus find that high purity materials may not be essential for obtaining high J_c values in the Ag/BPSCCO tapes/wires. These tapes prepared using commercial grade low purity (98–99%) materials have $J_c = 6{\cdot}14 \times 10^3\,\mathrm{A{\cdot}cm^{-2}}$ (77 K) and $1{\cdot}49 \times 10^5\,\mathrm{A{\cdot}cm^{-2}}$ (4·2 K). Optimization of the sintering parameters and the use of single phase 2223 material is expected to yield still higher J_c values at 77 K. Detailed studies are required to understand the role of excess copper and the presence of small iron impurity in increasing the J_c.

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