

Role of processing in improving the critical current of Ag/BPSCCO tapes

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Abstract. Silver-clad tapes of high T_c Bi-Pb-Sr-Ca-Cu-O superconductors have been fabricated through the powder-in-tube method. The critical current density, J_c , of a thick tape was $534 \text{ A}\cdot\text{cm}^{-2}$ (77 K, 0 T). Subsequent rolling and sintering of the tapes led to a gradual decrease in J_c , instead of the expected increase. This was caused by the microcracks developed in the core material by a rather drastic reduction during the rolling of the tapes. A modified and well controlled rolling technique, on the other hand, resulted in much improved J_c values. Repeated rolling and sintering resulted in a good grain alignment and no microcracks were observed. In the present studies, maximum J_c of $1846 \text{ A}\cdot\text{cm}^{-2}$ (77 K, 0 T) and $2.43 \times 10^4 \text{ A}\cdot\text{cm}^{-2}$ (4.2 K, 0 T) have been obtained. Optimization of the processing and sintering parameters are expected to lead to still higher J_c values.

Keywords. Critical current density; silver-clad tapes; sintering; BPSCCO system.

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1. Introduction

The most promising area of application of high T_c superconductors is the superconducting magnet technology for which the material is to be produced in the form of wires or tapes with high conducting metal cladding (Sharma *et al* 1988). The critical current density (J_c) of the Ag-clad wires of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ remained confined to a few times $10^3 \text{ A}\cdot\text{cm}^{-2}$ at 77 K (Kawashima *et al* 1989). With magnetic field, J_c drops precipitously to very low values. Besides the problems of low density, granular nature and weak links between the grains, peculiar to all the oxide superconductors, the YBCO system is extremely sensitive to the oxygen stoichiometry which is difficult to maintain in these wires/tapes during the sintering. Another problem typical of the Ag-clad YBCO wires is the low melting point of silver (940°C in presence of oxygen) which is the same as the sintering temperature required for YBCO. The discovery of superconductivity in the Bi-system by Maeda *et al* (1988) raised fresh hopes of developing high T_c wires as the Bi-system needs much lower sintering temperature ($840\text{--}880^\circ\text{C}$) and the sintering is usually carried out in air instead of oxygen. The

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Bi-system has two superconducting phases with T_c above 77 K, namely, the so-called high T_c phase with stoichiometry $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223) and the low T_c phase with stoichiometry $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ (2212) having $T_c = 110$ K and 80 K respectively. The low T_c phase has already proved its potential as a high field material for application at 4.2 K. J_c as high as $1.4 \times 10^5 \text{ A}\cdot\text{cm}^{-2}$ (4.2 K, 25 T) by Kase *et al* (1990) and $1.5 \times 10^4 \text{ A}\cdot\text{cm}^{-2}$ (4.2 K, 26 T) by Heine *et al* (1989) have already been reported for Ag-clad Bi-2212 tapes and wires prepared by the doctor blade and powder-in-tube technique respectively. For 77 K operation, it is, however, essential to develop Ag-clad wires/tapes using the 2223 phase BSCCO material as it has a T_c of 110 K well above the operating temperature (77 K). Addition of Pb, of course, is required (Green *et al* 1988) to obtain an increased fraction of the 2223 phase. Flexible ribbons of BPSCCO (2223 composition) prepared by the doctor blade technique with $T_c = 107$ K yielded a J_c value of $1850 \text{ A}\cdot\text{cm}^{-2}$ (77 K, 0 T) when a process of combined rolling and sintering was employed (Togano *et al* 1989). The repeated rolling and sintering process has been found effective in obtaining highly textured grains of the high T_c (2223) material by Asano *et al* (1989). A highest value of $J_c = 3560 \text{ A}\cdot\text{cm}^{-2}$ (77 K, 0 T) was achieved in high T_c bulk material by the authors. A J_c value of $5 \times 10^3 \text{ A}\cdot\text{cm}^{-2}$ (77 K, 0 T) has been reported by Sekine *et al* (1988) in a 2223 BPSCCO tape (after the copper sheath was removed) prepared by a combination of cold work and sintering.

It thus appears that the repeated rolling and sintering is required to obtain high density, well oriented grains and consequently high J_c in the 2223 phase material. In view of the potential applications of these materials in technology, indigenous development of high T_c superconducting wires/tapes is extremely important.

In this paper, we report our results on J_c of a variety of Ag-clad tapes of BPSCCO system which were prepared by the usual powder-in-tube method. This technique is the most viable one to produce long lengths of wires and tapes. Our results show that a significant improvement in J_c is possible by following a proper processing technique. It has thus been possible to obtain a zero field J_c of $1846 \text{ A}\cdot\text{cm}^{-2}$ at 77 K and $24300 \text{ A}\cdot\text{cm}^{-2}$ at 4.2 K in Ag-clad BPSCCO tapes. The optimization of the process parameters are expected to yield much higher J_c values.

2. Experimental

Materials with two different compositions, namely $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (series 1) and $\text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_{1.8}\text{Ca}_2\text{Cu}_{3.2}\text{O}_x$ (series 2) were prepared by the usual solid state reaction technique. The required quantities (as per formula units) of Bi_2O_3 (99.99%), PbO (99.99%), $\text{Sr}(\text{NO}_3)_2$ (99.9%), CaCO_3 (99.99%) and CuO (99.99%) were thoroughly mixed and ground. The mixture was calcinated in air at 810–820°C for 40 h twice with an intermediate grinding. The calcined powder was pulverized and pelletized. These pellets were sintered in air at 845°C for 72 h and furnace cooled. The pellets were ground back to powder form and packed in Ag tubes with O.D. = 10 mm and I.D. = 7 mm. The composite tubes were cold-rolled into the form of tapes of various thickness (tables 1 and 2). The tapes were air-sintered finally at 840–845°C for 10 to 115 h in air and slow cooled. A number of sintered tapes were rolled and sintered twice in air (series 1) as well as in a mixture of argon and oxygen (12:1) (series 2). The calcination and sintering were carried out in a programmable furnace following a definite heating and cooling schedule (Rajput *et al* 1991). The tapes of series 2

material were processed using a modified rolling technique. Tape specimens of series 1 were processed with rather large area reduction ratio of 10–30% per rolling. The modified rolling technique includes the use of cassette rollers each consisting of three alternate horizontal and vertical groove rollers giving an area reduction of 2–10% per rolling. Below a diameter of 1.5 mm the wires were flat rolled to a minimum thickness of 0.18 mm. The thickness reduction during each rolling was kept typically 0.01 mm. A short low temperature annealing after every 30% area reduction was employed. The minimum core thickness of the series 1 tapes was 0.1 mm and that of the series 2 tapes was 0.02 mm.

The transport critical current (I_c) was measured by a standard four-probe technique defined as a current producing a voltage of $1 \mu\text{V}/\text{cm}$. The J_c was then calculated by dividing I_c by the area of cross section of the core. The microstructure was studied by obtaining SEM pictures of the polished surfaces of the tapes. To study the grain morphology SEM photographs were also obtained on the fractured surfaces of the tapes of series 2. Room temperature XRD spectra were obtained on bulk material and also on the wide surface of the tapes (nos 7 and 9) after tripping of the silver sheath.

3. Results and discussion

The purpose of studies on the tapes of material of series 1 was two fold. One, to prepare the tapes with different core thicknesses and to see if the reduction of the core thickness leads to an increase of J_c as reported by Kawashima *et al* (1989) and by Okada *et al* (1988). Two, to subject the tapes to intermediate rolling and sintering which is reported (Mimura *et al* 1989 and Kumakura *et al* 1990) to be an effective technique for improving J_c values through grain orientation. Table 1 gives the details of the processing, reaction, core thickness and the J_c values measured at 77 K and 0 T of the 15 tape specimens of the series 1 material ($\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$). Five tape specimens of different thicknesses (samples 1 to 5) were prepared by the ordinary cold rolling technique. All these tapes were sintered at 840°C for 106 h and were characterized for T_c , J_c and microstructure.

It is seen from table 1 that with repeated rolling and sintering the J_c values of all the tape specimens are reduced systematically. The detailed microstructural studies carried out on these specimens reveal the presence of cracks in the core material with the reduction of the core thickness and during repeated rollings. Figure 1 (A, B and C) show typical SEM pictures of the polished surfaces (longitudinally) of the tape specimens 1A, 2A and 2B respectively. It is apparent from figure (1A) that the core (0.87 mm) of the tape does not have cracks and also shows a certain amount of grain alignment. As the core thickness is reduced, sample 2A (with core thickness of 0.46 mm) shows large cracks along the length and the gaps at the interface between the oxide core and the Ag-sheath. The J_c consequently drops from a value of $534 \text{ A}\cdot\text{cm}^{-2}$ (77 K) for specimen 1A to $135 \text{ A}\cdot\text{cm}^{-2}$ (77 K) for the sample 2A. The specimen 2A when rolled further to a core thickness of 0.38 mm (sample 2B) isolated oxide clusters with large voids in between are observed. J_c drops still to a lower value of $93.5 \text{ A}\cdot\text{cm}^{-2}$ (77 K). Increased cracks in the core material and lower J_c values are observed in all other specimens as indicated in table 1.

The SEM studies thus confirmed beyond doubt that our processing of the tapes was rather drastic. A modified rolling technique as discussed above was

Table 1. Parameters of the Ag-clad $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ tapes (series 1).

| Sample no. | Rolling and sintering details | | | | | |
|------------|-------------------------------|---------------------|--------------------|--------------------|--|-------|
| | Rolling no. | Core thickness (mm) | Reaction* (in air) | I_c (77 K) (Amp) | J_c (77 K) ($\text{A}\cdot\text{cm}^{-2}$) | |
| 1 | A | First | 0.87 | X | 14.5 | 534 |
| | B | Second | 0.62 | Y | 3.5 | 145.8 |
| | C | Third | 0.48 | Z | 1.25 | 58.7 |
| 2 | A | First | 0.46 | X | 3.0 | 135 |
| | B | Second | 0.38 | Y | 2.15 | 93.5 |
| | C | Third | 0.29 | Z | 0.8 | 41.7 |
| 3 | A | First | 0.27 | X | ** | — |
| | B | Pressed | 0.27 | Y | 2.75 | 159.2 |
| | C | Second | 0.18 | Z | 1.5 | 115.3 |
| 4 | A | First | 0.175 | X | ** | — |
| | B | Pressed | 0.175 | Y | 0.25 | 17.8 |
| | C | Second | 0.153 | Z | 0.26 | 20.8 |
| 5 | A | First | 0.14 | X | ** | — |
| | B | Pressed | 0.14 | Y | 0.5 | 140 |
| | C | Second | 0.11 | Z | 0.38 | 33.3 |

*X = $840^\circ\text{C} \times 106\text{ h}$; Y = $X + 845^\circ\text{C} \times 115\text{ h}$; Z = $Y + 845^\circ\text{C} \times 51\text{ h}$

**Tape swollen

therefore adopted for the tape specimens of the material of composition $\text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_{1.8}\text{Ca}_2\text{Cu}_{3.2}\text{O}_x$ (series 2). As discussed in detail the degree of area reduction was kept low in this technique. A schedule of intermediate vacuum annealing was also followed. The processing of this composite tube was carried out at the NRIM, Japan, during a brief visit of one of us (RGS). Table 2 gives the core dimensions, sintering conditions and the J_c values at 77 K and 4.2 K of the 9 specimens of the series 2. Figures 2 and 3 give the experimental critical current (I - V) plots obtained at 77 K and 4.2 K respectively for these 9 specimens. The J_c values are significantly higher than those obtained for the series 1 specimens. The J_c values are listed against each specimen. The improvement in J_c has been made possible by a good grain alignment obtained in these specimens and the absence of cracks. These results can briefly be summarized as below:

1. The J_c of the tapes (sample nos 1–3) air sintered only once increases with the decrease of core thickness. The J_c value increases from $400\text{ A}\cdot\text{cm}^{-2}$ to $1310\text{ A}\cdot\text{cm}^{-2}$ at 77 K as the core size is reduced from 0.059 mm to 0.034 mm. There is a corresponding increase in J_c at 4.2 K also.
2. Sintering in reduced oxygen atmosphere, that is, in a mixture of $\text{Ar}:\text{O}_2$ (12:1) increases the J_c at 77 K and at 4.2 K still further (sample nos 4 and 5).
3. Specimens 1, 2 and 3, when rolled again and sintered in $\text{Ar}:\text{O}_2$ (12:1) display higher J_c values at 77 K and 4.2 K. These specimens are designated as sample nos 6, 7 and 8 respectively in table 2. The highest value of J_c at 77 K is $1846\text{ A}\cdot\text{cm}^{-2}$ obtained for sample no. 7 with a core thickness of 0.029 mm.
4. Tape specimen no. 3 with a core thickness of 0.034 mm has a J_c of $1310\text{ A}\cdot\text{cm}^{-2}$

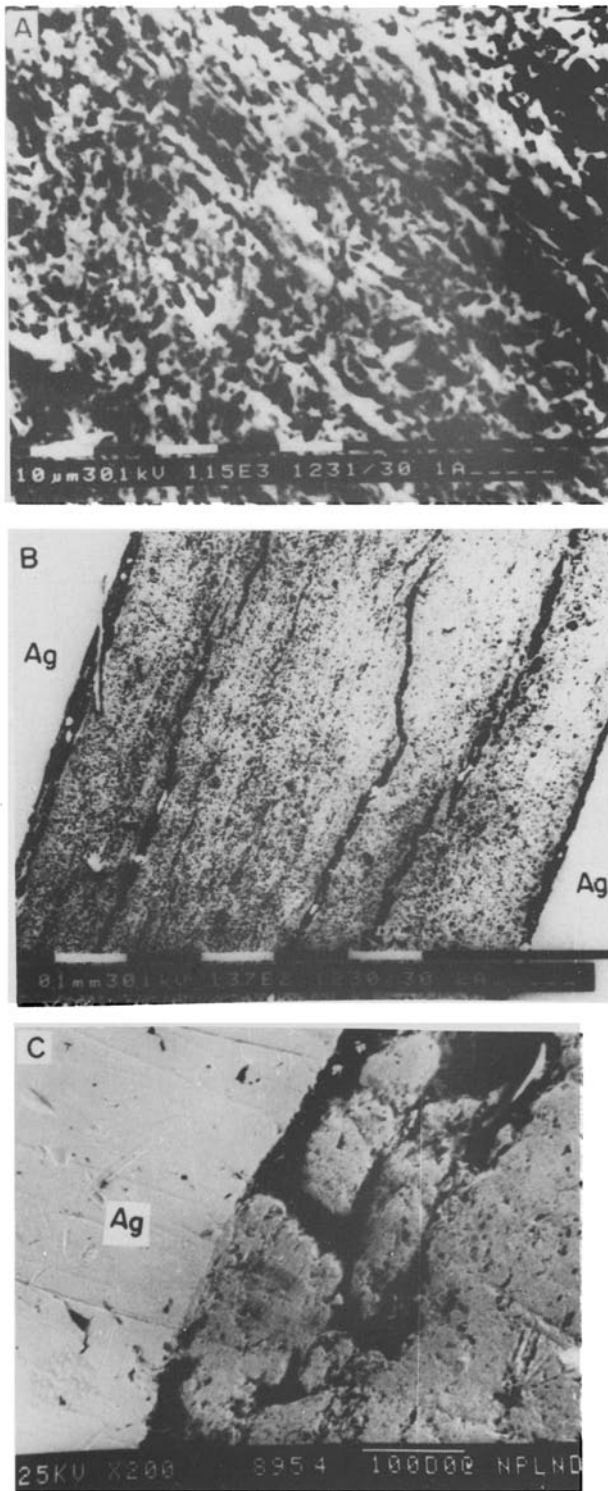


Figure 1. SEM picture taken longitudinally on the polished surfaces of the tapes. (A)–sample 1A; (B)–sample 2A and (C)–sample 2B as listed in table 1. Cracks are observed in figures (B) and (C).

Table 2. Parameters of the Ag-clad $\text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_{1.8}\text{Ca}_2\text{Cu}_{3.2}\text{O}_x$ tapes (Series 2). Air sinter ($845^\circ\text{C} \times 10\text{h}$); Ar sinter ($845^\circ\text{C} \times 10\text{h}$); Ar: $\text{O}_2 = 12:1$.

| Sample no. | Air sinter | | | Air sinter + Ar sinter | | | Air sinter + roll + Ar sinter | | | | |
|------------|---------------------|------------------------------------|---------|------------------------|------------------------------------|---------|-------------------------------|------------------------------------|---------|-------|--------|
| | Core thickness (mm) | $J_c(\text{A}\cdot\text{cm}^{-2})$ | | Sample thickness (mm) | $J_c(\text{A}\cdot\text{cm}^{-2})$ | | Sample thickness (mm) | $J_c(\text{A}\cdot\text{cm}^{-2})$ | | | |
| | | (77 K) | (4.2 K) | | (77 K) | (4.2 K) | | (77 K) | (4.2 K) | | |
| 1. | 0.059 | 400 | 7500 | — | — | — | 6. | 0.029 | 1050 | 18900 | |
| 2. | 0.056 | 520 | 9500 | — | — | — | 7. | 0.029 | 1846* | 18300 | |
| 3. | 0.034 | 1310 | damaged | 4. | 0.034 | 1410 | 15600 | 8. | 0.021 | 1500 | 22600 |
| — | — | — | — | 5. | 0.031 | 990 | 15000 | 9. | 0.020 | 1360 | 24300* |

*Highest J_c values at 77 K and 4.2 K

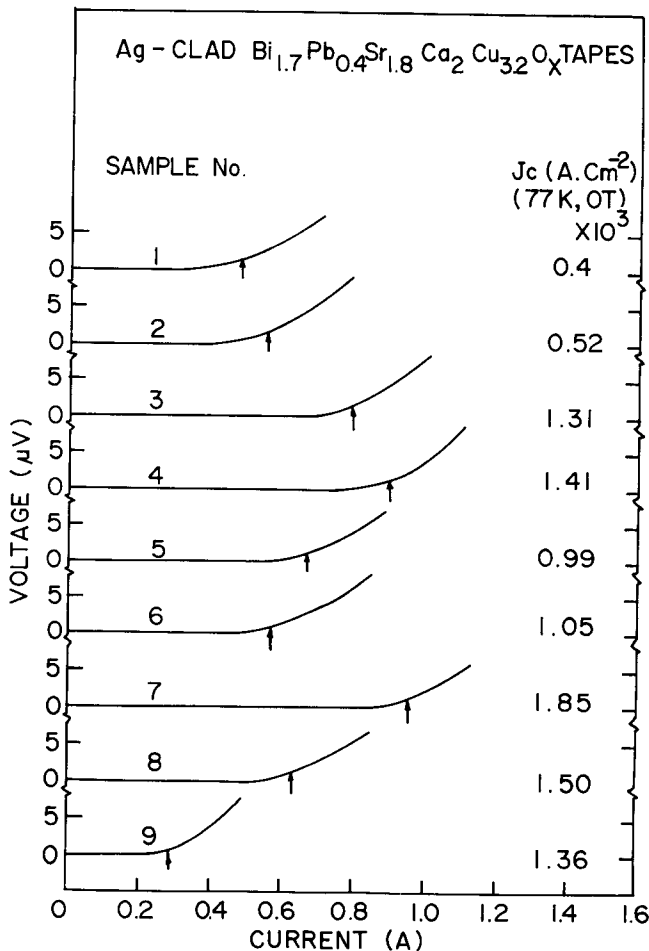


Figure 2. I-V plots of Ag-clad $\text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_{1.8}\text{Ca}_2\text{Cu}_{3.2}\text{O}_x$ tapes (series 2 specimens). The specimen No. and J_c values ($1\ \mu\text{V}/\text{cm}$) at 77 K are indicated against specimen.

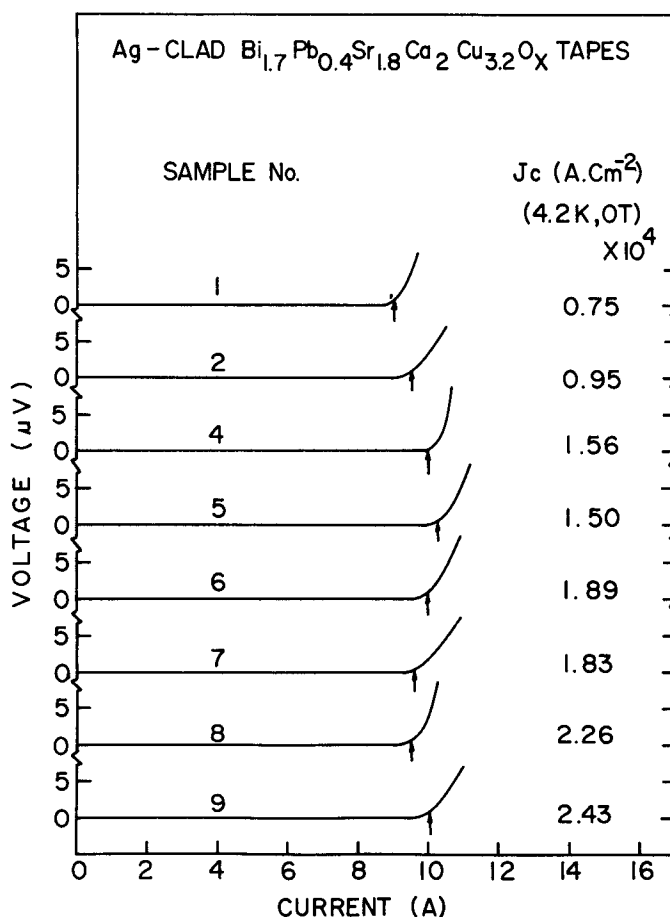


Figure 3. I-V plots of Ag-clad $\text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_{1.8}\text{Ca}_2\text{Cu}_{3.2}\text{O}_x$ tapes (series 2 specimens). The specimen No. and the J_c values ($1 \mu\text{V}/\text{cm}$) at 4.2 K are indicated against specimen.

at 77 K when sintered in air ($845^\circ\text{C} \times 10 \text{ h}$). It increases to $1410 \text{ A}\cdot\text{cm}^{-2}$ when sintered again ($845^\circ\text{C} \times 10 \text{ h}$) in $\text{Ar}:\text{O}_2$ (12:1) (sample no. 4). The same tape when rolled again to a core thickness of 0.021 mm and Ar sintered, J_c increases further to $1500 \text{ A}\cdot\text{cm}^{-2}$ (sample no. 8).

5. Sample no. 5 with a core thickness of 0.031 mm sintered in air ($845^\circ\text{C} \times 10 \text{ h}$) followed by the $\text{Ar}:\text{O}_2$ sintering ($845^\circ\text{C} \times 10 \text{ h}$) has a J_c of $990 \text{ A}\cdot\text{cm}^{-2}$ at 77 K. This value increases to $1360 \text{ A}\cdot\text{cm}^{-2}$ when rolled to a core thickness of 0.02 mm and sintered in $\text{Ar}:\text{O}_2$ ($845^\circ\text{C} \times 10 \text{ h}$), sample no. 9.

6. The J_c values at 4.2 K are 10 to 19 times the values at 77 K. The highest value of J_c at 4.2 K is $24300 \text{ A}\cdot\text{cm}^{-2}$ for sample no. 9.

The grain structure of the core material of the sintered tapes was studied by obtaining the SEM pictures on their fractured cross sections. Figure 4 shows the grain structure of the specimen nos 1, 2, 4 and 8 with a core thickness of 0.059 mm, 0.056 mm, 0.034 mm and 0.021 mm respectively. It is seen from figure 4 that sample no. 1 with a core thickness of 0.059 mm and a least value of $J_c = 400 \text{ A}\cdot\text{cm}^{-2}$ has no grain alignment. Grain alignment improves as the core size is reduced during

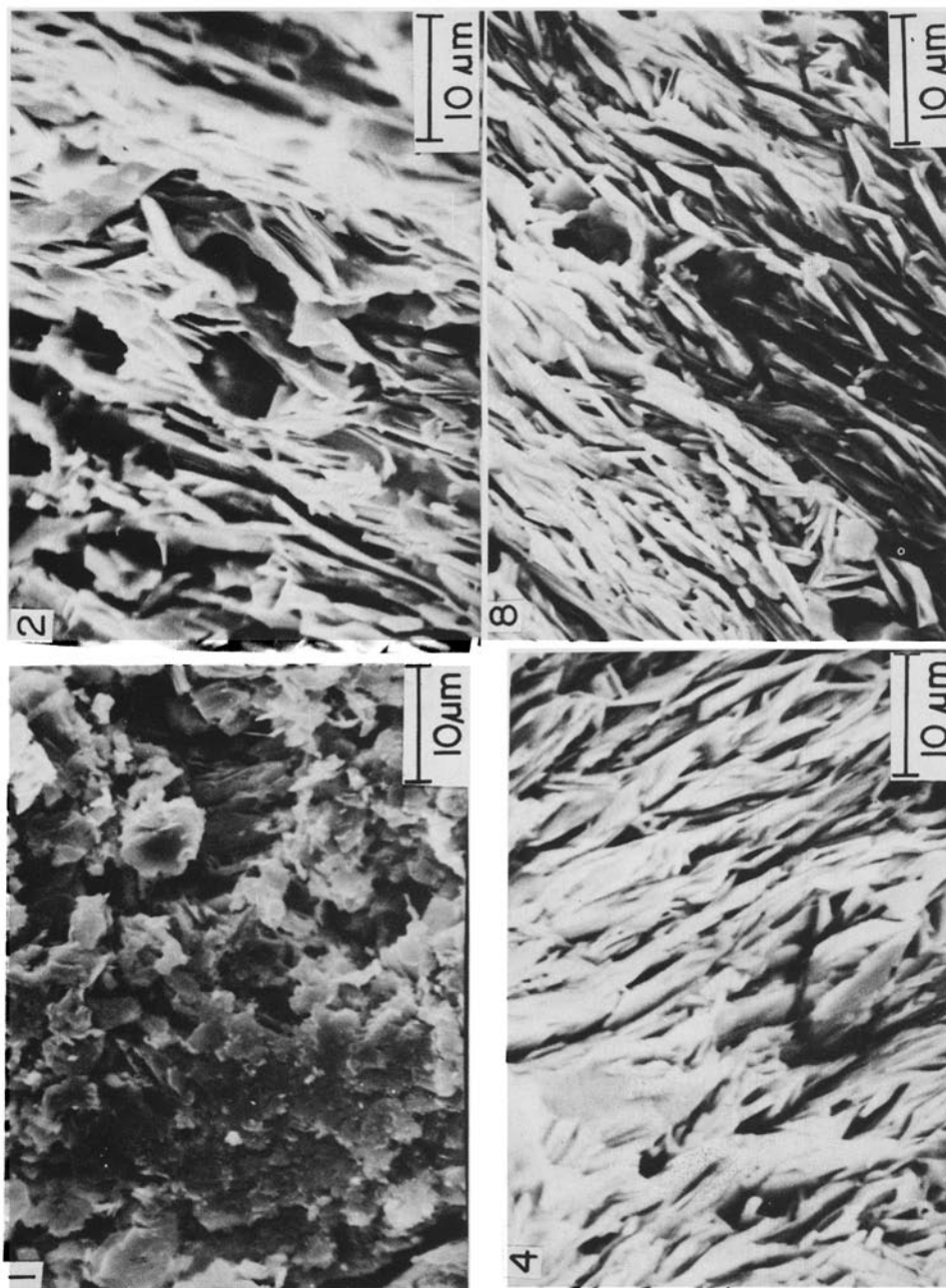


Figure 4. SEM pictures taken on the fractured cross sections of the tape specimens 1, 2, 4 and 8 with core thicknesses 0.059 mm, 0.056 mm, 0.034 mm and 0.021 mm respectively. Grain alignment is found improving with the reduction of the core thickness.

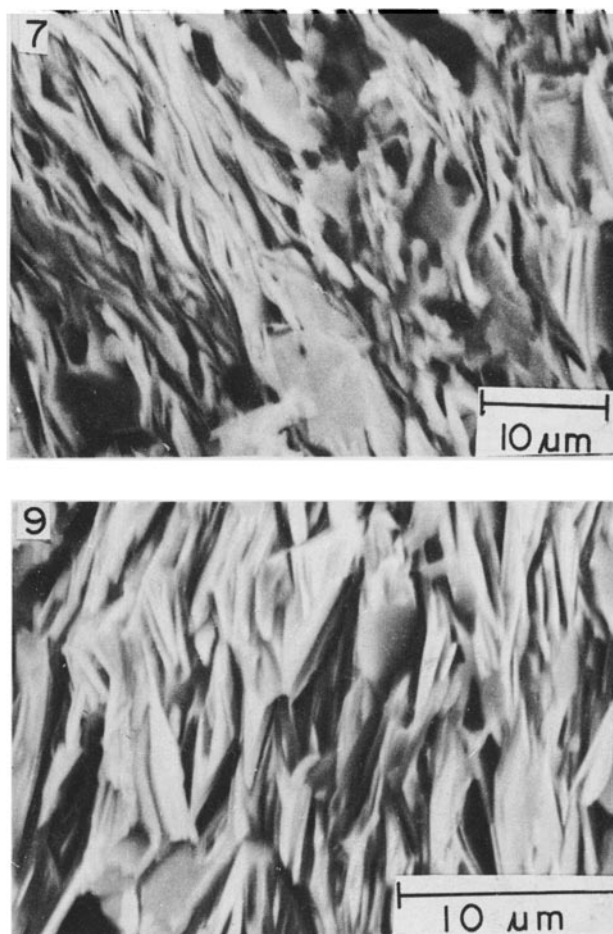


Figure 5. Grain alignment as shown by the SEM on the fractured surfaces of the tape specimens 7 and 9 with best values of J_c at 77 K and 4.2 K respectively. Specimen 9 seems to have best grain alignment.

successive rollings. Sample nos 2, 4 and 8 thus have J_c 520, 1410 and $1500 \text{ A}\cdot\text{cm}^{-2}$ respectively at 77 K. Similar trend of increasing J_c with reduced core size is observed at 4.2 K. Figure 5 shows the grain structure of sample nos 7 and 9 which are characterized by highest J_c values at 77 K and 4.2 K respectively. Both the specimens have good grain alignment. Specimen no. 9 has by far the highest degree of grain alignment and the highest J_c value at 4.2 K, that is, $2.43 \times 10^4 \text{ A}\cdot\text{cm}^{-2}$.

Room temperature XRD spectra were recorded on the bulk material used for the series 2 specimens as well as on the core material of the tape specimens 7 and 9. These spectra are reproduced in figures 6 and 7 respectively. The spectra on the tape specimens were recorded by tripping of the silver sheath from one side of the tape. Since the core material thickness was too small a number of silver peaks are observed in the XRD patterns of the tapes as seen in figure 7. Two things are noteworthy, one that the starting bulk material contains about one third of the low T_c (2212) phase as determined by the ratio of the intensities of the (002) reflections of the two phases,

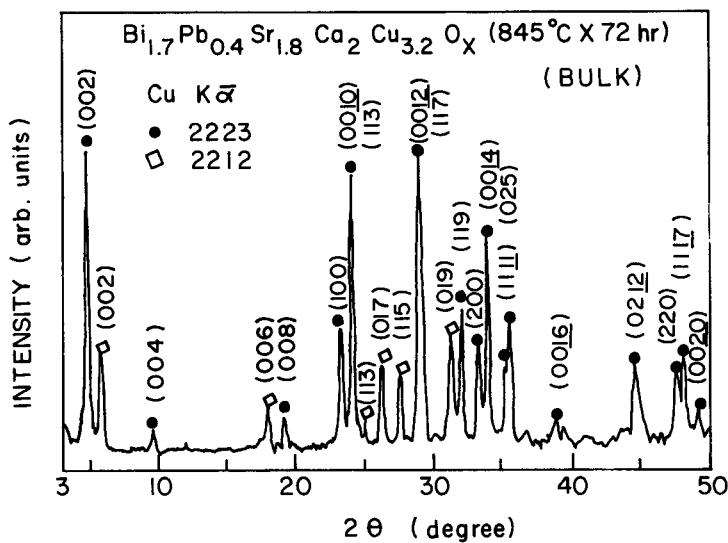


Figure 6. Room temperature XRD spectra of the bulk material used for the series 2 specimens. The intensity ratios of the (002) peaks for the high T_c and the low T_c phases give the fractions of the two phases as 3:1.

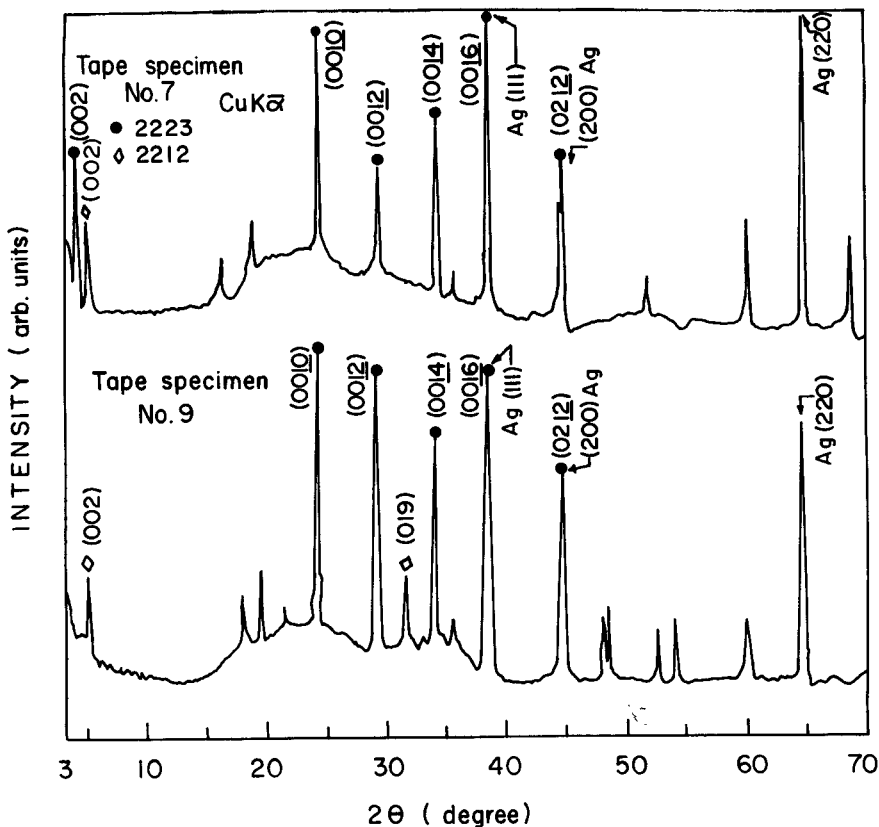


Figure 7. The XRD spectra of the core material of the tape specimens 7 and 9 taken after the tripping of the Ag sheath. The (00l) reflections in the two specimens are sharp indicating the alignment of the c -axis. Ag peaks are shown by arrows.

as seen in figure 6. The fraction of the low T_c phase, of course, is reduced in the tape specimens as seen in figure 7. Two, that the (00l) reflections of samples 7 and 9 have become very sharp. This is an indication that the grains in these specimens are aligned along the c -axis.

Table 2 also shows that the J_c values of the specimens 6–9 at 4.2 K do not scale strictly with the J_c values at 77 K. Two reasons are possible for such a behaviour. One could be that the material contains a small fraction of the low T_c (2212) phase which is known to carry larger critical current at 4.2 K (Kase *et al* 1990). The dominant component, of course, is the high T_c (2223) phase in our tape specimens. This is evident from the XRD patterns (figure 7) and is also confirmed by the fact that we observe an improvement in J_c consequent upon intermediate rolling and sintering. It has indeed been shown by Kumakura *et al* (1990) that intermediate rolling and sintering leads to an increase of J_c of the 2223 phase only and not of the 2212 phase. The second reason for the J_c values at 77 K and 4.2 K not scaling with each other could be that the J_c -measurements at 77 K and 4.2 K were carried out in two separate runs using two different probes. It is possible that some of the samples got strained during handling and resoldering these specimens. J_c values under such a situation may not scale at two temperatures (4.2 K and 77 K).

These studies indicate that high J_c values are indeed possible in Ag-BPSCCO tapes by choosing a good combination of processing, sintering and a proper sintering atmosphere. Final sintering of the high T_c phase material under reduced oxygen pressure appears to be a crucial parameter for obtaining high J_c . We have recently found (Rajput *et al* 1991) that the sintering atmosphere necessary for the 110 K phase formation could vary drastically (right from vacuum to oxygen) depending upon the stoichiometry of the compound and the amount of Pb-addition. These studies conclusively show that a reduced/partial oxygen pressure enhances the 110 K phase up to a small addition of Pb. For large Pb-additions sintering in oxygen becomes necessary. Our sintering parameters in the present studies have not been optimized as yet. These studies are in progress now. The indications are that the J_c values in fresh lot of tapes prepared will far exceed the present J_c values.

4. Conclusions

The modified rolling technique with small area reduction ratios has enabled us to obtain higher J_c values in the Ag-clad BPSCCO tapes. The process of repeated rolling and sintering leads to an increase in J_c through grain alignment and an increase in bulk density. Reduced oxygen pressure during final sintering leads to still high J_c values. The highest J_c values obtained in the Ag/BPSCCO tapes are $1846 \text{ A} \cdot \text{cm}^{-2}$ at 77 K and $24300 \text{ A} \cdot \text{cm}^{-2}$ at 4.2 K. Optimization of processing and sintering parameters are in progress which are expected to yield still higher J_c values.

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