

Zone melting–refining in Bi–Pb–Sr–Ca–Cu–O superconductor prepared through the sol–gel method

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A zone melting–refining technique, with a horizontal sample-holding pattern for incorporating grain orientation in sintered bismuth-based superconductor (BPSCCO) is presented. Acrylate precursor-derived BPSCCO powder was uniaxially compacted into strips of 60 mm × 10 mm × 2 mm and sintered at 845 °C for 20 h to obtain 90% density. These strips were zone melted in a three-zone furnace which had an independent temperature control system for each zone. The grain orientation in the sample was studied by scanning electron microscopy and X-ray diffraction. In the case of a BPSCCO–Ag (5%) composite, the silver was seen to flow along the intergranular boundaries of the BPSCCO grains. The present technique is an easy and fast method to introduce orientation of grains with large aspect ratio into sintered BPSCCO or Ag–BPSCCO composite under partial melting–refining conditions. The possibility of extending the present technique to silver-sheathed wire and tapes is also indicated.

1. Introduction

Bismuth-based ceramic superconductors, discovered by Maeda *et al.* [1], have been found to be most interesting in comparison to other ceramic counterparts [2, 3], primarily due to the high T_c value of 110 K, as well as the less-stringent processing parameters. This family of compounds could carry high currents owing to the appreciable difference between T_c and the boiling point of nitrogen. However, the very long heat-treatment time is a real difficulty in arriving at phase-pure $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$, also known as 2223 phase. But the addition of lead as a partial substituent at the bismuth site in $(\text{BiPb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ decreased the processing time considerably, and increased the stability of this phase [4]. Sol–gel methods resulting in molecular mixing of starting material [5, 6], as well as microwave decomposition techniques [7], resulting in reactive powders, reduced the total processing time.

The current-carrying capacity, J_c , is a factor of the texturing of grains in ceramic superconductors. Again, the large anisotropy existing in crystals of these compounds, and the random orientation of grains, always leads to a low value of J_c . It has been established that in ceramic superconductors such as BPSCCO, the maximum amount of current is carried along the a – b plane and hence an a – b plane orientation of all the grains is the ultimate requirement [8]. Superconductors with texturing possess high J_c and are essential for the development of wire and tapes fabricated by the oxide-powder-in-tube (OPIT) process for practical applications [9]. Textured high- T_c materials have

been successfully developed by melt texturing [10] and quench–melt techniques in BPSCCO and YBCO systems. The texturing of YBCO grains has been reported by Kumakura *et al.* [11] in tapes fabricated by the doctor-blade technique, and a directional solidification by vertical [12] and horizontal sample-holding arrangements [13] have already been reported. The present report relates to the introduction of texture in sintered BPSCCO through a repeated zone melting–refining technique, which has also been extended to Ag–BPSCCO composites.

2. Experimental procedure

A precursor powder, obtained by decomposing a gel derived from a mixture of nitrates of bismuth, lead, strontium, calcium and copper in the ratio 1.6:0.4:2:2:3 respectively, and acrylic acid, was heat treated to prepare 110 K phase-rich bismuth-based superconductor. Details of experimental procedures have been discussed earlier [5]. A similar set of samples was also prepared by adding silver nitrate to the initial composition to obtain 5% Ag in the final composite.

The BPSCCO superconductor, as well as the composite powders, were ball milled separately for 12 h in hexane using cylindrical zirconia as grinding media in polyvinyl chloride containers. The slurry was filtered, dried and uniaxially compacted into 60 mm × 10 mm × 2 mm sized strips under a pressure of 150 MPa. These strips were sintered at 845 °C for 20 h, and then subjected to zone melting in a three-zone furnace apparatus (Fig. 1) with furnace movement at 30 mm h⁻¹. The sample was kept on a platinum plate inside a static alumina tube of 250 mm diameter.

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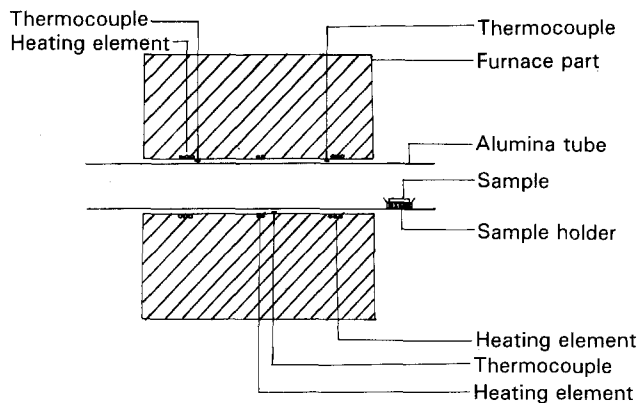


Figure 1 The zone-melting apparatus.

The three zones of the furnace were independently controlled to result in premelting (750 °C), melting (845–860 °C) and cooling (750 °C) zones. Table I briefly describes the different conditions adopted for zone melting. Strips were repeatedly zone melted up to five times at the optimum temperature conditions. The microstructural features of as-sintered and zone-melted samples were observed under an SEM (Jeol 35C, Japan). Identification of the phases and orientation were noted by X-ray diffraction (XRD, Rigaku, Japan). Similar experiments were repeated using Ag-BPSCCO composite strips.

3. Results and discussion

The three heating zones of the zone-melting furnace were well separated in order that diffused heating was minimized. The width of the melting zone was 1 cm and other zones were kept 2 cm apart from the central zone. The temperature distribution inside the alumina tube has a profile as given in Fig. 2, which can be varied as required. A temperature difference of 100 °C was maintained between zones in order to minimize convection heating and to keep a distinct gradient between the melting zone and adjacent ones. Adjustments in the cooling zone also provided a slow mode of cooling the partially melted BPSCCO to enhance the texturing. BPSCCO superconductor is sensitive to melting near the sintering temperature and hence has

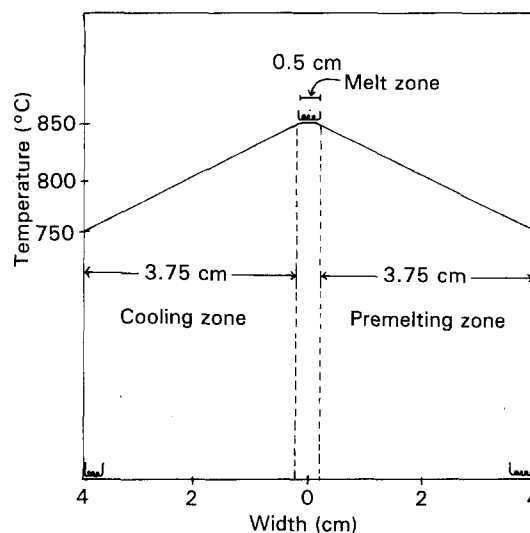


Figure 2 Temperature profile in the zone-melting apparatus.

only a narrow range of stability, the maximum temperature being 860 °C [14], beyond which it undergoes decomposition to different binaries or ternaries and individual oxides. Hence the usual sintering temperature of BPSCCO superconductor is kept around 845 °C. Fig. 3a shows the randomly arranged BPSCCO grains in an as-sintered strip sample in the range 845–850 °C. Particularly under zone-melting experiments, it is still possible to subject this strip to higher temperatures because the exposure time is very short. The sample remains in the melting temperature region only for 10 min. The optimum conditions for melting and the accompanying zones were arrived at by following the microstructural and XRD data on samples subjected to different conditions. A fractograph of a sample heated to above 855 °C (Fig. 3b) showed additional phases apart from the high T_c BPSCCO flakes. The sample heated to above 860 °C failed to exhibit even the Meissner effect. On the contrary, heat treatment at 845 °C did not show any visible microstructural variation from the sintered sample. Based on these observations, the zone-melting temperature in the present investigation was fixed at 850 °C with pre- and post-melting zones at 750 °C (Table I).

TABLE I Standardization of zone-melting conditions

No.	Pre-melting zone temp. (°C)	Melting zone temp. (°C)	Cooling zone temp. (°C)	SEM observation after first run
1	750	845	750	No change in the microstructure
2	750	850	750	Partial grain alignment
3	750	855	750	Partial grain alignment + partial decomposition
4	750	860	750	Destruction of platelets of BPSCCO superconducting grains

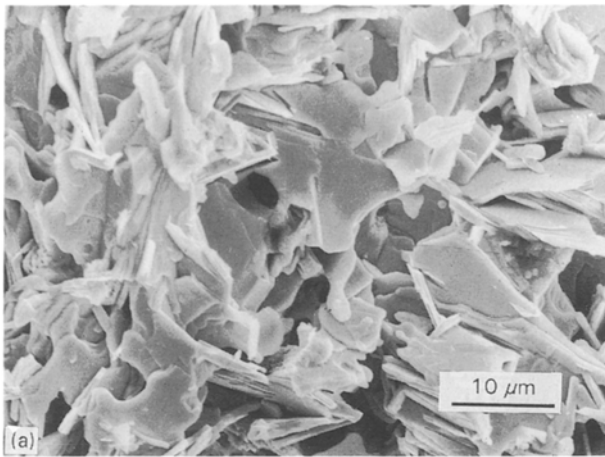


Figure 3 Microstructure of (a) sintered BPSCCO strips, and (b) strips heat-treated at 860 °C.

Fig. 4a–c show the microstructural evolution in samples during repeated zone melting for the first, third and fifth times. One important point to be stressed here is that the grain alignment is along the direction of zone movement which is as demonstrated in Fig. 5. Although this phenomenon of grain alignment is difficult to explain, liquid-phase-assisted sliding of the grains, dissolution and crystallization in a preferential direction at the melt–solid interface may be some possibilities.

XRD patterns of as-sintered and zone-melted samples are given in Fig. 6. Zone-melted samples show substantial orientation effects from the sintered BPSCCO. The zone-melted BPSCCO for five repeated runs (Fig. 6b) shows reflection from (001) planes of 2223 grains. A similar oriented pattern is observed in samples polished down to half the thickness. The fractograph of zone-melted samples shows large plates arranged one over the other, thus indicating that the orientation effect has spread through the bulk of the sample. Further, the zone-melted BPSCCO sample gave XRD peaks corresponding only to (001) planes of the 2223 phase, though the starting material also contains around 10% 2212 phase also. Thus, after the fifth run, i.e. total 50 min exposure at the melting zone, textured pure 2223 phase was found. Thus the total process may be termed a zone melting–refining and the refining is

based on the concept of the differential rate of movement of the different phases under thermal-drag conditions and it should be possible to extend it to the separation of the high- T_c phase from a mixture, owing

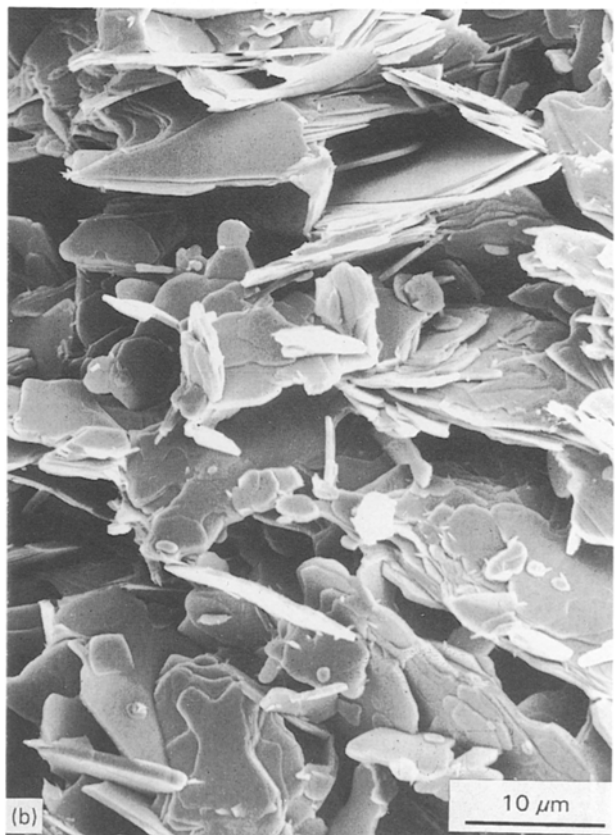
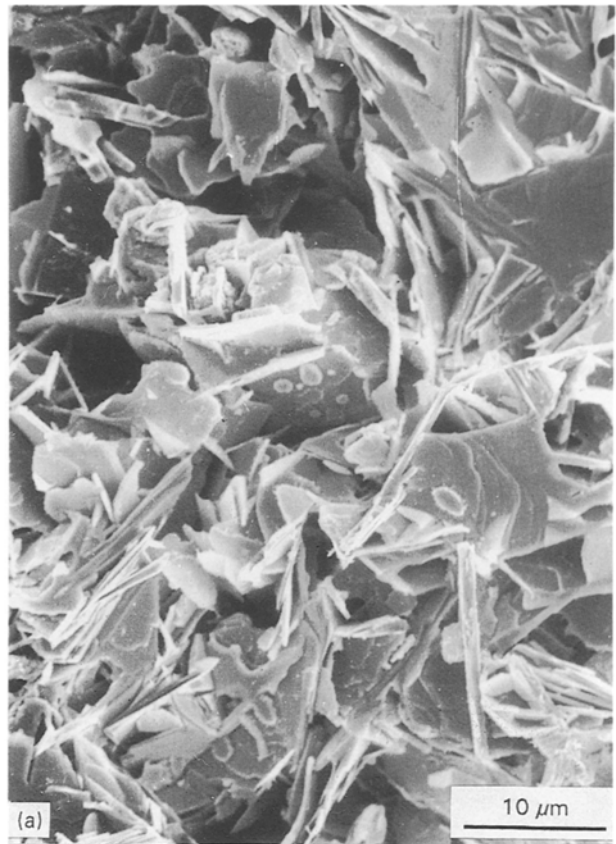


Figure 4 Microstructural evolution in BPSCCO strips after repeated zone melting: (a) first run, (b) third run and (c) fifth run; (d) finishing end of the strip.

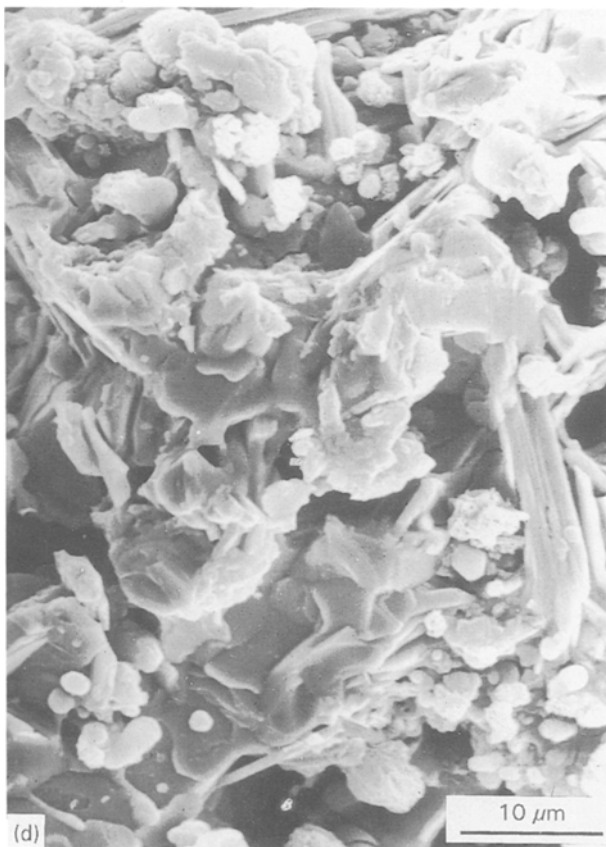
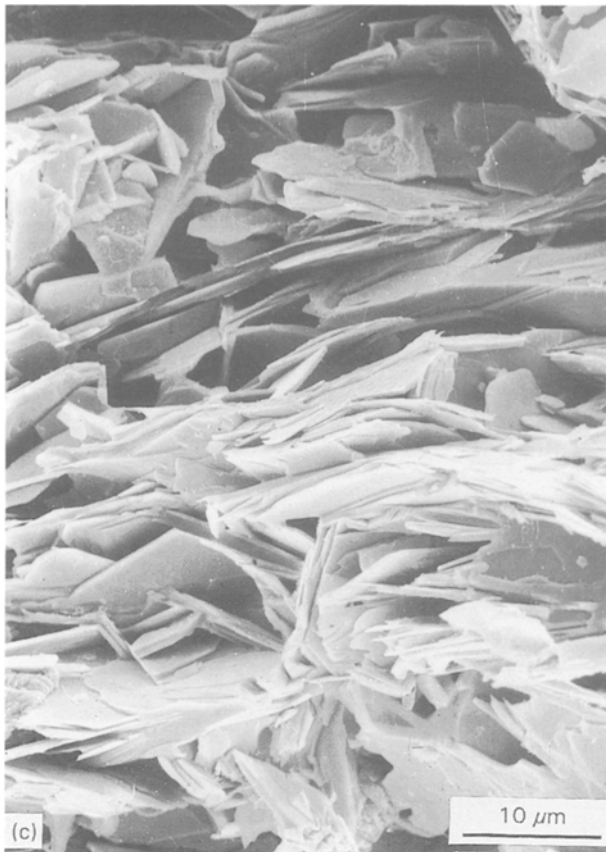


Figure 4 Continued.

to the difference in their melting temperatures. In the present study, the rear end of the BPSCCO strip had a microstructure having near spherical grain morphology (Fig. 4d), different from the characteristic 2223

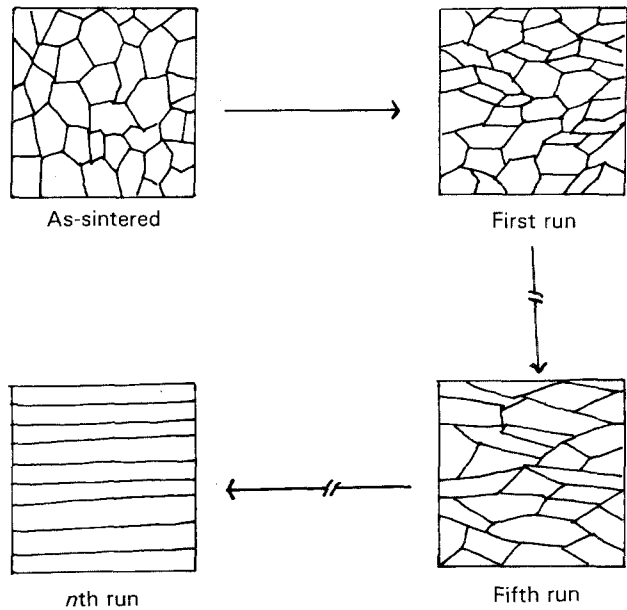


Figure 5 Pictorial representation of grain alignment in BPSCCO strips.

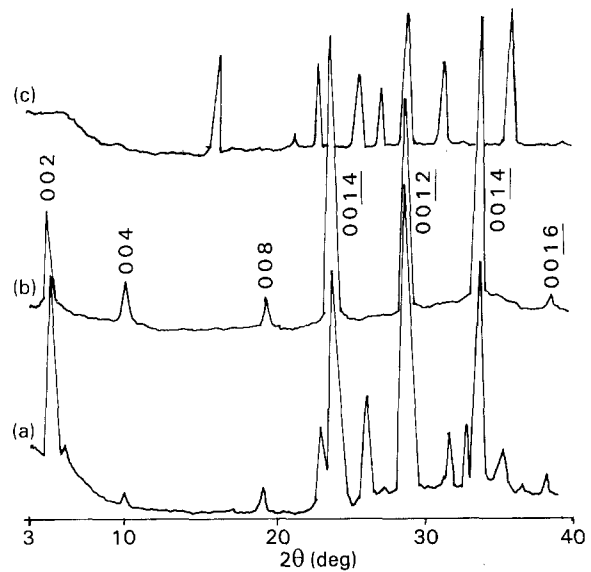


Figure 6 XRD patterns of (a) random, and (b) *a-b* plane-oriented strips, and (c) from the rear end of a zone-melted strip.

phases, and was confirmed from the XRD pattern to contain impurity phases (Fig. 6c).

The zone melting–refining could also be a technique not only useful to arrive at oriented grain structure in BPSCCO, but also to produce grains with very large aspect ratios. By strictly adjusting the heat-treatment conditions, it is possible to grow grains to sizes larger than 50 μm. Microstructural features also show that the refinement can be uniformly effected throughout the bulk of the samples, and not only on the surface. 5% Ag–BPSCCO composite strips subjected to the zone-melting operation showed a rather uniform distribution of silver along the grain boundaries of the textured BPSCCO (Fig. 7). However, isolated regions are observed where silver particles are segregated. Possibly this occurs in regions inhomogeneous distribution of silver in the composite sample subjected to zone melting. Silver acts as connecting link between

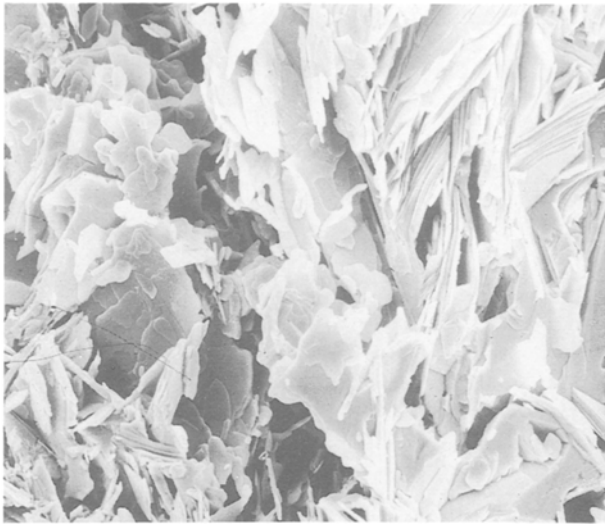


Figure 7 Fractograph of 5% Ag BPSCCO composite after zone melting.

long BPSCCO grains, which may enhance the mechanical and electrical properties of the bulk superconductor. Because the present system is a horizontal loading one, and also the refinement is spread through the bulk of the sample, as seen from the SEM fractograph, this method could be extended to longer samples. Further, because silver is indicated to become aligned along the boundaries of the BPSCCO grains, this could also provide the possibility of refining silver-sheathed BPSCCO tapes.

4. Conclusion

A zone melting-refining technique using a three-zone heat-treatment system with a horizontal sample-loading pattern, has been shown to be successful in achieving desirable textured grain structure in BPSCCO superconductors having an initial random grain-oriented microstructure. By adjusting the pre-melting, melting and cooling zones judiciously, it is further possible to segregate the impurity phases and thus enrich the high T_c phase. This method has been extended to 5% Ag-BPSCCO composite and the possibility of distributing the ductile phase along the BPSCCO grain boundaries is proved. Together with the horizontal sample-holding facilities for long tapes, the refinement possible in the bulk of the superconductor and the possibility of aligning the ductile

phase along the grain boundaries, the present method indicates the scope for post-sintered processing of wires and tapes.

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