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Double-step lamination of grain-oriented Y–Ba–Cu–O superconducting ceramics

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The uniformity of grain alignment and anisotropic superconducting properties were investigated in laminated tape-cast $YBa_2Cu_3O_{7-x}$ ceramics. Large, platey $YBa_2Cu_3O_{7-x}$ grains were prepared by gentle grinding of pellets prepared by liquid-phase sintering. A mixture of pre-reacted $BaCuO_2$ and CuO was added as a molten flux. The grain-oriented specimens were then prepared by tape-casting followed by lamination and sintering. A high degree of grain orientation was observed near the surface of the specimen. Successive polishing and X-ray diffraction studies revealed that the effective depth of the oriented layer was approximately 200 μm. The small anisotropy observed in the critical current density calculated from the magnetization provided additional evidence for the non-uniformity of the grain alignment across the sample. By reducing the thickness of the laminated sample to the effective depth for obtaining a uniform structure, polycrystalline ceramic samples with a homogeneous and high degree of grain orientation were obtained by a double lamination method.

1. Introduction

Ceramic superconductors [1–4] have highly anisotropic (layered) crystalline structures and anisotropic superconducting properties. In $YBa_2Cu_3O_{7-x}$ (more commonly known as the 123 superconductor), markedly anisotropic superconducting properties have been measured on single crystals [5–9]. In particular, the critical current density, J_c, in the *a–b* plane and along the *c* axis of the perovskite 123 crystal structure differ by at least a factor of 20 [8, 9]. The current density J_c of single-crystal 123 samples is far superior to those observed in bulk ceramic bodies. Random grain orientation in polycrystalline ceramics was suggested as one of the major reasons for this low J_c [10].

Based on these observations, it is desirable to obtain grain-oriented structures in bulk ceramic samples. Special techniques including hot pressing [11], sinter-forging [12] and magnetic field-aligning [13] have made it possible to produce polycrystalline samples with textured structures. Even in conventionally sintered samples, enhancement of the preferred *c* orientation has been observed [14–16]. However, Bhalla *et al.* [17] have noticed that the grain orientation is strong only near the sample surface where *c* plates are highly oriented to a depth of about 100 μm. The low value of anisotropy in magnetization J_c observed in grain-oriented samples [14, 17] suggests the possibility of non-uniform texture throughout the bulk samples.

In a previous study [18], it was demonstrated that grain alignment could be obtained with large-grain 123 powder using tape-casting and high-pressure lamination. In this study, anisotropic behaviour in magnetic susceptibility and magnetization J_c are reported for these specimens. In order to determine the degree of grain orientation, the anisotropy value of the observed magnetic properties is compared with those of single crystals. Successive polishing and corresponding X-ray diffraction studies are also used to investigate the uniformity of the texture. A modified lamination technique is described for the preparation of uniformly textured polycrystalline superconductors.

2. Experimental procedure

Grain-oriented superconducting specimens were prepared by a technique similar to that described in an earlier paper [18]. To obtain large and platey grains in the powder, a liquid-phase sintering technique was used. The starting composition was 91 wt % $YBa_2Cu_3O_{7-x}$–7 wt % $BaCuO_2$–2 wt % CuO. The 123 compound was prepared by a citrate method, as described in the earlier paper [18]. The pre-reacted $BaCuO_2$ powder was prepared by the conventional ball-milling and calcining method. The mixed powders were pressed under 150 MPa to form a thin rectangular bar with dimension of 1.2 cm × 2.5 cm × 0.2 cm. The green pellets were sintered in air at 950 °C for 10 h, and then ground gently in a mortar and pestle. Powder size and morphology were evaluated using SEM.

Thin sheets of the plate-like superconducting powder were fabricated by tape-casting, using a commercially available binder (Cerbind 73140, Metoramics Technology Inc., San Marcos, California). The thickness of the dried green tape was approximately 130 µm. Tape-cast sheets 3 and 20 layers thick were laminated with a pressure of 600 MPa at room temperature. After burning out the binder, the specimens were sintered at 950 °C in air for 24 h on ZrO_2 substrates. The sintered specimens were then heat-treated in an O_2 atmosphere at 500 °C for 10 h.

The degree of grain orientation was determined by X-ray diffraction. The diamagnetic properties were measured using an a.c. inductance bridge [19]. The magnetization versus applied field measurements were performed using a vibrating-sample magnetometer.

3. Results and discussion

As reported in the previous study [18], the grain coarsening occurring during sintering resulted in 123 grains having anisotropic (platey) morphology. The presence of a liquid phase during the sintering stage resulted in faster grain growth and more regular grain morphology. Grain alignment through tape-casting could be obtained with this large grain powder. Fig. 1 shows the morphology of 123 particles obtained after gentle grinding of sintered pellets whose starting composition was 91 $(YBa_2Cu_3O_{7-x})$–7$BaCuO_2$–2CuO (wt %). The pre-reacted $BaCuO_2$ and CuO acts as a molten flux at the sintering temperature and promotes

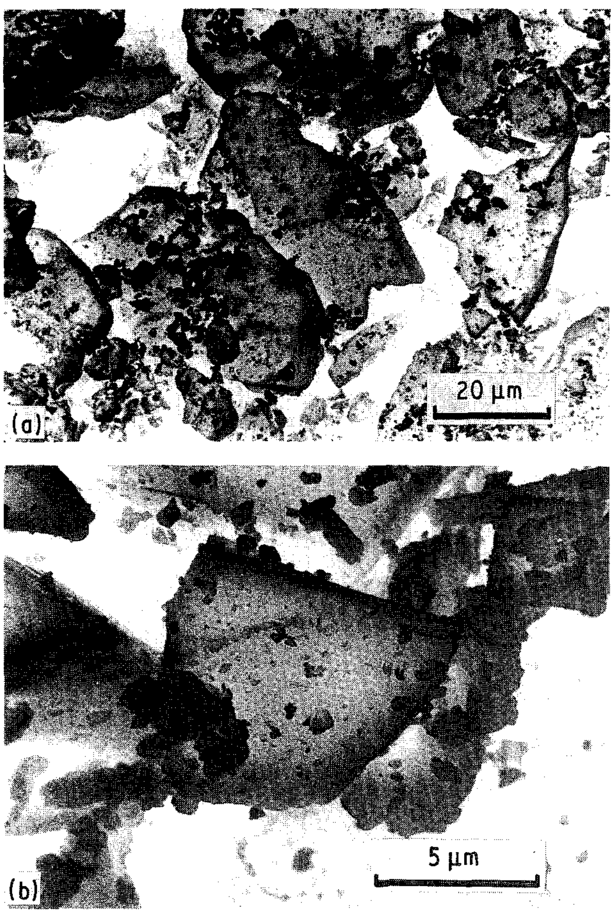

Figure 1 The morphology of ground powders from liquid-phase sintered pellets: (a) at low magnification and (b) at high magnification.

the growth of 123 grains. The resulting 123 powder exhibited distinct thin plate morphology (see Fig. 1). The size of the large grains, approximately 20 µm across and 5 µm thick (Fig. 1a), is nearly the same as those observed in the sintered pellets. Many small grains approximately 5 µm or less also maintained their platey morphology (Fig. 1b).

The anisotropy of 123 powder and specimens obtained after each processing step as determined by X-ray diffraction is presented in Fig. 2. The powder exhibited a typical X-ray diffraction pattern of the orthorhombic triple-perovskite unit cell. The diffraction peaks corresponding to the liquid phase (a mixture of $BaCuO_2$ and CuO) were not detected within the resolution of the X-ray diffraction. However, direct observation of the microstructure of sintered pellets revealed a thin glassy phase at the grain boundary, believed to be $BaCuO_2$ and CuO.

Though the 123 grains had a thin platey morphology, there was little increase in *c*-axis alignment after tape-casting. However, substantial enhancement of *c*-axis orientation was observed after lamination with the preferred *c* axis parallel to the pressing direction. As described in the previous paper [18], uniaxial pressing during lamination is critical for obtaining a textured structure. Partially oriented platey 123 grains are rearranged preferentially with their large surfaces perpendicular to the pressing axis. Further slight enhancement in *c*-axis orientation took place during sintering due to densification and grain growth. The intensity summation ratio of $0\,0\,l$ peaks to all $h\,k\,l$ peaks, $\Sigma 0\,0\,l/\Sigma h\,k\,l$, which can be taken as a measure of *c*-axis orientation, is 0.7 for this sintered specimen.

Anisotropic behaviour of the magnetic properties was investigated in the highly grain-oriented specimens. Fig. 3 shows the temperature dependence of a.c. magnetic susceptibility determined both parallel and perpendicular to the preferred *c* axis. The T_c observed in both directions is 91 K, which is consistent with the resistive T_c [18]. A sharp drop in magnetic susceptibility was observed near the transition temperature, with

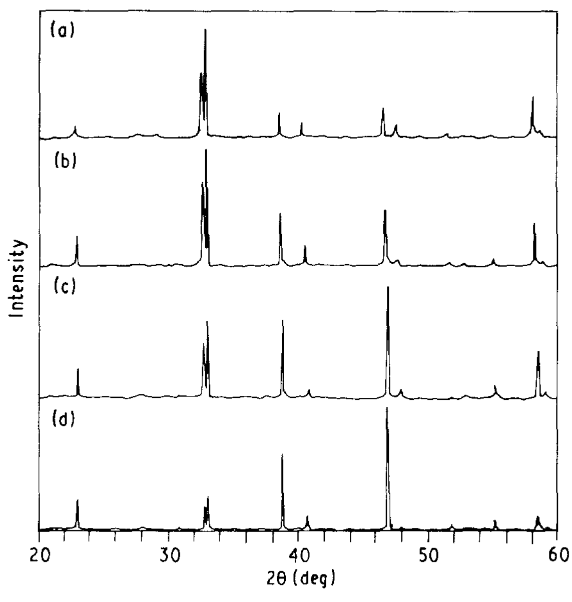

Figure 2 X-ray diffraction patterns of (a) powder, (b) tape-cast films, (c) laminates, and (d) sintered specimen.

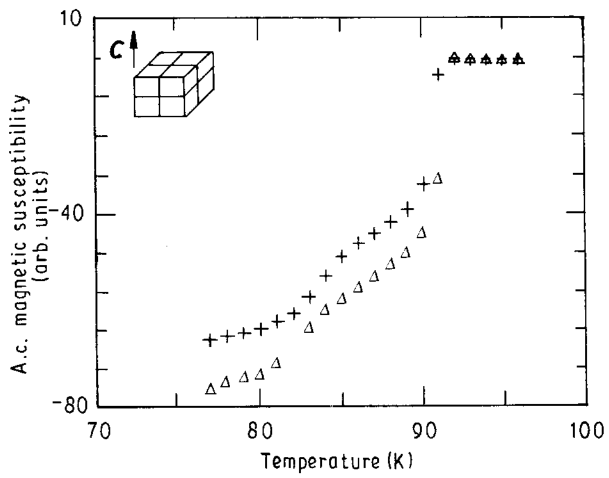

Figure 3 Magnetic susceptibility versus temperature behaviour observed in the sintered laminated specimen: (△)$H \parallel C$, (+) $H \perp C$.

the slope further reduced beyond a certain inflection point in both directions. This behaviour is thought to be due to the weak-link coupling between the superconducting grains [20]. Partial penetration of magnetic flux through the second phase (especially flux-additive in this study) at the grain boundaries will bring about diamagnetic loss and, therefore, result in a decrease in the real component of the susceptibility. A more detailed explanation of this behaviour will be given in a later paper [21]. Anisotropy in the magnetic susceptibility was, however, evident far below T_c. The diamagnetic susceptibility with the applied field parallel to the c axis was found to be about 1.2 times that measured perpendicular to the c-axis.

The magnetization curve of the textured sample was measured with a vibrating-sample magnetometer at 4.2 K. Fig. 4 shows the complete hysteresis loops (due to irreversibility in magnetization) traced up to 90 kOe with the applied field parallel and perpendicular to the preferred c axis. The overall shape of the loop is very similar in both directions, with an anisotropy evident in magnetization M. The magnitude of the magnetic moment with the applied field parallel to the preferred c axis was found to be about twice that of the perpendicular field. The magnetization J_c, which is proportional to the magnetization hysteresis at a particular field, also showed anisotropy of the same magnitude. Similar anisotropic behaviour in magnetization J_c has been observed in the grain-oriented polycrystalline samples produced by sinter-forging [12] and magnetic field-aligning [13].

As stated earlier, single-crystal studies have shown that there is a strong anisotropy in resistivity [5], Meissner signal [6] and magnetization J_c [8, 9]. In particular, the anisotropic nature of the electronic structure of this layered compound was demonstrated in critical-field and critical current measurements performed on single crystals. Dinger *et al.* [8] reported in their magnetic measurements that the magnetization J_c exhibited an anisotropy of 20 at zero field and it became still larger with increasing applied fields. Even taking into account the degree of grain alignment of this specimen (0.7 determined by X-ray diffraction), the observed anisotropy in magnetization J_c was too small compared to that of a single crystal. Therefore, uniformity in the grain orientation throughout the bulk sample was suspected. The degree of uniformity was investigated by successive polishing and corresponding X-ray diffraction studies. Fig. 5 shows the X-ray diffraction patterns observed on the sample surface and a polished plane about 200 µm below the surface. In contrast to the strong texturing ($\Sigma 0 0 l / \Sigma h k l = 0.7$) on the surface, only weak texturing ($\Sigma 0 0 l / \Sigma h k l = 0.4$) was observed on the polished plane. Further successive polishing revealed diffraction patterns similar to that observed on the original tape-cast films (see Fig. 2b). The effective depth to which the uniaxial symmetry texture was formed was estimated to be about 200 µm on both sides of the specimen. As found in this study, the weak anisotropy observed in magnetization J_c of other reported textured samples [12, 17] suggests that there

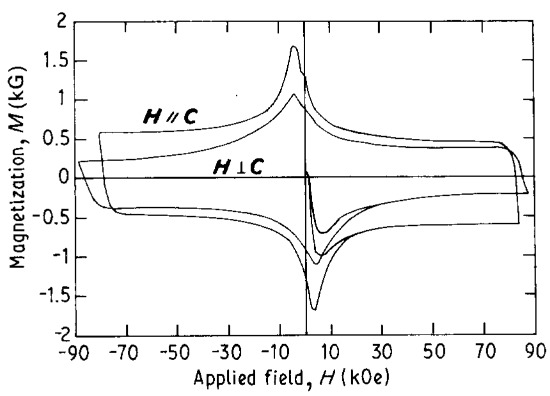

Figure 4 Magnetization versus applied magnetic field behaviour observed in sintered laminated specimen at 4.2 K.

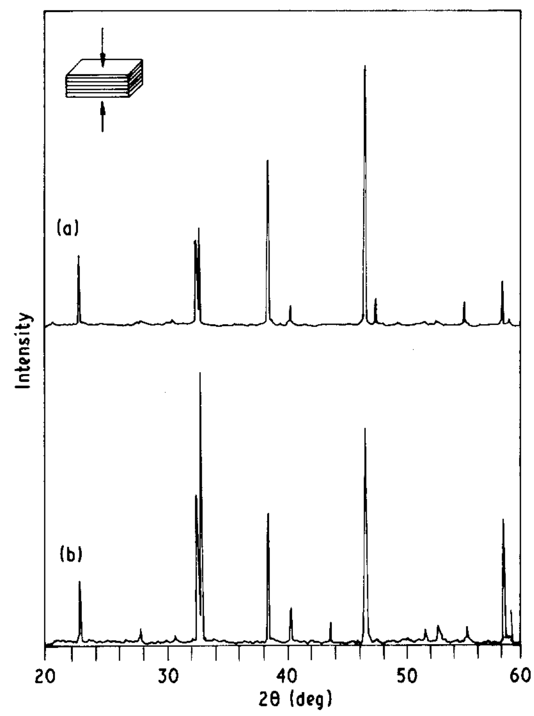

Figure 5 X-ray diffraction patterns of a single laminated and sintered specimen: (a) surface and (b) polished plane.

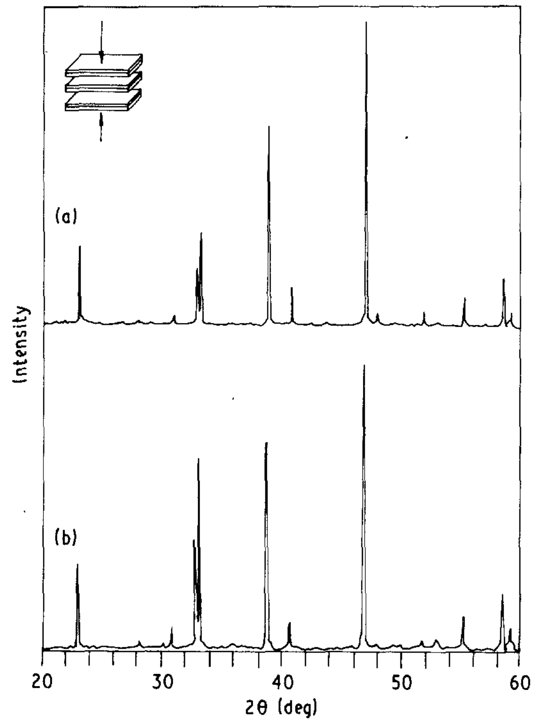

Figure 6 X-ray diffraction patterns of a double-step laminated and sintered specimen: (a) surface and (b) polished plane.

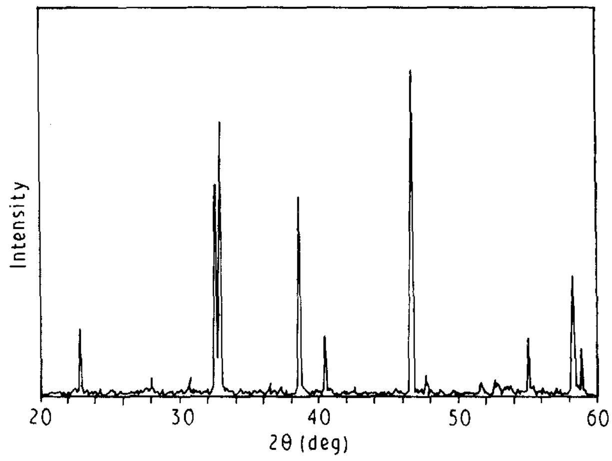

Figure 7 X-ray diffraction pattern of tape-cast film of which binder content is 50 wt % and thickness is 80 μm.

was a strong possibility of non-uniform grain orientation (localized in the surface region) in those samples as well.

Based on the above results, the thickness of a laminated specimen was reduced to the effective depth for obtaining a uniform grain-oriented structure. Since the thickness of the dried green tape was 130 μm, a three-layer lamination should provide a sample with uniform texture. If these preforms are then laminated again with several other triple sheets, relatively thick and uniformly textured polycrystalline samples are obtained. As demonstrated in Fig. 6, successive polishing and X-ray diffraction studies revealed that strong *c*-axis orientation was uniform throughout the thickness of a double-step laminated and sintered specimen 0.1 cm thick.

It is important to obtain the high degree of grain alignment in the tape-cast film itself. In the present study, only weak texture was observed in the tape-cast films even though relatively large-grain $YBa_2Cu_3O_{7-x}$ powder was used. However, some modification to the rheologic conditions of the casting slurry can bring about a higher degree of grain orientation. Preliminary study has shown that grain alignment increases with lower solid loadings in the binder and by reducing the doctor blade height. For instance, a cast film with 50 wt % binder and a thickness of approximately 80 μm exhibited relatively strong texture ($\Sigma 0\,0\,l / \Sigma h\,k\,l = 0.5$) as shown in Fig. 7. However, the fired multilayer density was too low (65% of theoretical) and, therefore, weak strength and low critical current density were expected. In fabricating grain-oriented specimens with a high density using tape-casting, not only the morphology of the grains is important but their size and aspect ratio as well.

4. Conclusion

The results of this study demonstrate that uniformly textured $YBa_2Cu_3O_{7-x}$ superconducting ceramics can be obtained by double-step lamination of tape-cast films. In the case of a single laminated specimen, the strong *c*-axis orientation (due to rearrangement of plate-shaped 123 grains in the binder matrix under uniaxial pressure) was observed only in the surface region. Because of this localized textured structure, the observed anisotropy value of magnetization critical current density was small compared to that of single crystals. Successive polishing and corresponding X-ray diffraction revealed the effective depth of layer in which a high degree of preferred orientation was formed to be approximately 200 μm. If the thickness of initial laminated specimen was reduced to this size, a uniform texture could be produced throughout the specimen. By successive lamination of several layers of these preforms, relatively thick and homogeneously textured superconducting samples were prepared. Strong $0\,0\,l$ X-ray diffraction peaks were observed not only on the surface but also in the interior of this double-step laminated specimen.

Several attempts have been made to fabricate grain-oriented superconducting wire by extruding the mixture slip of powder and polymer binder [22, 23]. In this process, grain orientation can be produced as a result of mechanical shear between the wire and die wall. However, as found for tape-casting, the texture or orientation is primarily formed on the wire skin. The wire diameter will thus have to be reduced to near that of the effective depth to obtain a homogeneously textured structure.

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