Effect of hot uniaxial pressing on the microstructure and critical current density of (Bi, Pb)-2223 tapes

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Abstract
Pressures up to 10 MPa were applied uniaxially to (Bi, Pb)₂Sr₂Ca₂Cu₃O₇₋ₓ ((Bi, Pb)-2223) tapes during either the first or second stage of the heat treatment process in air. After both annealing stages, an increase of the oxide filament density of the tapes was observed when applying pressure. For the first stage, the critical current (Ic) of the tapes was very sensitive to the applied pressure, and the reproducibility was poor. This behaviour is related to the large amount of liquid involved in the reaction. This liquid was easily pushed out from the centre to the edges of the tapes by pressure, which caused local deviations of the composition and hence, a decrease of volume fraction of (Bi, Pb)-2223. In contrast, applying pressure only during the second stage when a moderate amount of liquid is produced brought about the high densification and the reproducible enhancement of Ic and critical current density (Jc) values by about 40 and 100%, respectively. This enhancement is attributed to the high densification and improved coupling of grains due to the uniaxial pressure.

1. Introduction
Among the Bi-based high critical temperature (Tc) superconductors, described as Bi₂Sr₂Caₙ₋₁CuₙOₙ⁺₂ (Bi-22(n−1)n; n = 1, 2, 3), the Pb-substituted (Bi, Pb)₂Sr₂Ca₂Cu₃O₇₋ₓ ((Bi, Pb)-2223) phase shows the highest Tc of about 110 K. At present, the (Bi, Pb)-2223 phase is the most promising material for application to wires and tapes. Although Ag-sheathed (Bi, Pb)-2223 tapes show critical current density (Jc) values of about 75 and 30 kA cm⁻² for short and industrial lengths, respectively [1, 2], locally Jc reaches values as high as 250 kA cm⁻² over 50–100 μm long regions [3]. The reason for the degradation of Jc in long tapes is the presence of many voids and impurity phases, which act as obstacles for grain connectivity and hence, supercurrent path [4, 5]. In order to reduce porosity, intermediate rolling and/or pressing are carried out during the fabrication process. By rolling and/or pressing, many cracks are introduced, which cause a deterioration of Jc. These cracks are healed by subsequent heat treatment, but this process requires long time, and hence, increases the fabrication cost.

Recently high-pressure (HP) processing was performed with a hot isostatic pressing (HIP) furnace (∼200 MPa) to improve the density of oxide filaments of (Bi, Pb)-2223 tapes and to suppress the lead evaporation from the tapes [6–10]. Another possible benefit from adopting this technique is the shortening of the heat treatment time, i.e. to achieve single-step heat treatment without intermediate rolling or pressing. The density of the filaments was indeed improved, and the Jc was enhanced by HP processing. Alternatively, high densification of the oxide filaments can also be achieved by the application of uniaxial pressure. This is thought to increase Jc, also by an improvement of grain alignment. This can be achieved probably more effectively by applying pressure uniaxially rather than isostatically. Hot uniaxial pressing was recently improved for processing (Bi, Pb)-2223 bulk [11], and Jc values up to 20 kA cm⁻² at 77 K and 0 T were obtained under pressures up to 30 MPa [12]. As an alternative technique...
3. Results and discussion

3.1. First heat treatment stage

First we investigated the effect of pressure during the first stage (reaction thermal treatment). At this stage of processing, the precursor mixture reacts and forms the (Bi, Pb)-2223 phase via the formation of a transient liquid [15]. The $I_c$ distribution as a function of temperature in the tapes heat treated without pressure indicates that the $T_{\text{opt}}$ is 838 °C, as mentioned below. The $I_c$ values of tapes heat treated at 838 °C without pressure increased up to 14 A with increasing heat treatment time up to 50 h, and no $I_c$ improvement was observed for further annealing. This suggests that the phases present in the green tapes were almost converted to the (Bi, Pb)-2223 phase during this stage. Indeed, XRD patterns of these tapes indicated that the increment of the volume fraction of the (Bi, Pb)-2223 phase was very small for the heat treatment beyond 50 h.

SEM observations of the cross section of the tapes heat treated without pressure indicated that the microstructure was porous. In contrast, the densification of the oxide filaments was clearly observed in tapes heat treated under 1 MPa, as shown in figure 2. The overall thickness of these tapes was 300 and 240 μm for 0 and 1 MPa, respectively, whereas the width of the tapes was almost independent of pressure. This indicates that the application of uniaxial pressure is effective in increasing the filament density.

Figure 3 shows the $I_c$ distribution as a function of temperature for the tapes heat treated for 35 h under various pressures. Without pressure, $T_{\text{opt}}$ was found at 838 °C. The same $T_{\text{opt}}$ was obtained for 1 MPa, and an $I_c$ enhancement of about 20% was observed on average compared to 0 MPa. However, this enhancement was not systematically observed, and some tapes showed even a deterioration. On the other hand, the deterioration in $I_c$ was always observed under pressures above 1.5 MPa. The squeezing out of the liquid is responsible for the deterioration of $I_c$. Some oxides formed by the solidification of this liquid were indeed observed at both ends of these tapes. The loss of the liquid causes local deviations of the composition and hence, the increase in volume fraction of impurity phases. XRD patterns of these tapes indicated that the volume fraction of the (Bi, Pb)-2223 phase decreased with increasing pressures. During the first stage of the heat treatment, a large amount of liquid is produced when the (Bi, Pb)-2223 phase is formed from the pristine precursor powder. To avoid squeezing out the liquid, therefore,
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Figure 2. SEM images of the polished cross section of the tapes heat treated at 838 °C for 35 h under (a) 0 and (b) 1 MPa during the first stage.

Figure 3. $I_c$ distribution as a function of temperature for the tapes heat treated for 35 h under various pressures during the first stage. The $I_c$ values were recorded at 77 K and 0 T.

The pressure should be applied when a moderate quantity of liquid is present, i.e. during the subsequent annealing stage (second heat treatment stage).

Figure 4 shows the DTA curves recorded for the green tapes and the tapes heat treated at 838 °C for various times without pressure. Two endothermic peaks were present for the green tapes. The onset of the low-temperature peak related to the formation of liquid [16] corresponds to the $T_{opt}$ (~838 °C) chosen for the heat treatment. With increasing heat treatment time, the area of the low-temperature peak decreased, indicating the disappearance of the liquid in this temperature range. After heat treatments for more than 24 h, an almost complete disappearance of this peak was observed. On the other hand, the high-temperature peak shifted to higher temperatures due to the formation of the (Bi, Pb)-2223 phase. This is in agreement with the XRD patterns and the $I_c$ values of these tapes. With increasing heat treatment time, the increments of the volume fraction of the (Bi, Pb)-2223 phase and $I_c$ values of the tapes became smaller, as mentioned above. Therefore, for the second stage heat treatment, we used tapes which were heat treated at 838 °C for 50 h without pressure during the first stage.

3.2. Second heat treatment stage

Figure 5 shows SEM images of polished cross section of tapes heat treated at 838 °C for 35 h under various pressures during the second stage. Compared with the microstructure of the tapes heat treated without pressure during the first and second stages, the density of the oxide filaments was improved by the intermediate pressing, as shown in figures 2(a) and 5(a). However, the microstructure of the tapes after the second stage was still porous due to the further formation of the (Bi, Pb)-2223 phase during this stage. By applying pressures as low as 1 MPa during the second stage, the densification of the filaments was clearly observed. No voids were observed for the tapes heat treated under pressures above 3.5 MPa. The overall thickness of these tapes was 250, 220, 200 and 180 µm for 0, 1, 3.5 and 5.5 MPa, respectively. For these tapes, no traces of liquid squeezed out at the edges of the tapes were observed.

Figure 6 shows SEM images of etched cross section of the tapes shown in figure 5. The tapes heat treated without pressure showed a lower density compared with other tapes. For all the tapes, (Bi, Pb)-2223 grains near the interface region aligned
Figure 5. SEM images of polished cross section of the tapes heat treated at 838 °C for 35 h under (a) 0, (b) 1 and (c) 3.5 MPa during the second stage.

Figure 6. SEM images of etched cross section of the tapes heat treated at 838 °C for 35 h under (a) 0, (b) 1 and (c) 3.5 MPa during the second stage. The etchant used was a mixed solution of 1% perchloric acid and 99% 2-butoxyethanol.

parallel to the Ag filaments in these tapes. However, this alignment was interrupted by impurity phases such as alkali earth cuprates when far from the interface. The rocking curve measurements of these tapes indicated that the application of pressure did not improve grain alignment. The full-width at half maximum (FWHM) value of 0014 peaks in the XRD patterns was 9.8°, 10.1°, 10.1° and 9.8° for 0, 1, 4.3 and 5.5 MPa, respectively. The FWHM values of other 0010 and 0012 peaks did not decrease with increasing pressure, either, indicating that the grain alignment was not improved by pressure. The absence of pressure effect on the grain alignment is probably because substantial amount of impurity phases are present in these tapes as mentioned below. Therefore, the reduction of these impurity phases is expected to be more effective in improving grain alignment and hence, $J_c$.

Figure 7 shows the $I_c$ distribution as a function of pressure for the tapes heat treated at 838 °C for 35 h during the second stage. The $I_c$ value of 35 A was obtained without pressure. This is nearly three times as large as the values after the first stage heat treatment. With increasing pressures, the $I_c$ gradually increased up to 48 A at 5.5 MPa. This value corresponds to about 40% enhancement compared with the value obtained without pressure. Taking account of the cross section reduction due to the applied pressure, these values correspond to about 10 and 20 kA cm$^{-2}$ in $J_c$ for 0 and 5.5 MPa, respectively. Similar $J_c$ enhancement is observed for the tapes from other source which carries 35 kA cm$^{-2}$ at 77 K and 0 T [17]. It is noted that the application of higher pressure, 10 MPa, decreased the $I_c$ value by 37 A.

Figure 8 shows XRD patterns of the tapes heat treated at 838 °C for 35 h under various pressures during the second stage together with the tapes heat treated for 50 h without pressure during the first stage for comparison. Compared with the pattern of the tapes heat treated without pressure during the first and second stages, the volume fraction of the (Bi, Pb)-2223 phase increased when applying pressure during the second stage. The intensity ratio, $I((\text{Bi, Pb})-2223, 0014)/[I((\text{Bi, Pb})-2223, 0014) + I(\text{Bi-2212}, 008) + I(\text{Bi-2201}, 008)]$, of the XRD
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Figure 7. $I_c$ distribution as a function of pressure for the tapes heat treated at 838 °C for 35 h during the second stage. The $I_c$ values were recorded at 77 K and 0 T.

peaks of the (Bi, Pb)-2223, Bi-2212 and Bi-2201 phases, was 0.80 and 0.87 after the first and second stages, respectively. On the other hand, concerning the pressure effect on the tapes heat treated during the second stage, the above-mentioned intensity ratio of the XRD peaks was 0.87, 0.76, 0.74, 0.78, 0.77 and 0.75 for 0, 1, 1.8, 4.3, 5.5 and 10 MPa, respectively, indicating that the volume fraction of the (Bi, Pb)-2223 phase decreased by pressure.

Figure 9 shows the field dependence of $I_c$ values ($I_c(B)$) of the tapes heat treated at 838 °C for 35 h under 0, 5 and 5.5 MPa during the second stage. Here the $I_c(B)$ values are normalized to zero field value ($I_c(0)$). The drop of $I_c$ in a low-field region (<0.2 T) can be interpreted as an indication of weak links [18]. The tapes heat treated under pressures showed smaller field dependence in $I_c(B)/I_c(0)$ below 0.2 T. These results suggest that the $I_c$ enhancement shown in figure 7 is not due to the promotion of (Bi, Pb)-2223 formation but due to the improved coupling of grains by pressure.

For further increase in $J_c$ of the (Bi, Pb)-2223 tapes, the increase of volume fraction of the (Bi, Pb)-2223 phase is necessary. The current tapes heat treated under uniaxial pressure contain substantial amount of impurity phases, which act as obstacles for supercurrent path and grain coupling.

Figure 8. XRD patterns of the tapes heat treated at 838 °C for 35 h under (a) 0, (b) 1, (c) 1.8, (d) 4.3 and (e) 5.5 MPa during the second stage together with the pattern of the tape heat treated at the same temperature for 50 h without pressure during the first stage for comparison (f). The $I_c$ values of these tapes at 77 K and 0 T are shown in the figure. Here the XRD peaks of (Bi, Pb)-2223, Bi-2212 and Bi-2201 phases are marked by circles, rhombuses and squares, respectively.
alignment. Without impurity phases, uniaxial pressure can more effectively improve the grain alignment, and hence, further $J_c$ increase is expected.

4. Conclusions

Moderate pressures up to 10 MPa were applied uniaxially to (Bi, Pb)-2223 tapes during the first or second stage of the heat treatment process. The $I_c$ value of the tapes was very sensitive to the applied pressure for the first stage, and the reproducibility was poor. This is due to that the liquid was squeezed out from the edges of the tapes by pressure, which caused local deviation in composition and hence, decreased the volume fraction of the (Bi, Pb)-2223 phase. In contrast, after an almost complete conversion to the (Bi, Pb)-2223 phase occurring during the first stage, applying pressure during the second stage brought about reproducible enhancement of $I_c$ and $J_c$ values by about 40 and 100%, respectively. This enhancement is ascribable to the high densification of oxide filaments and the improved coupling of grains by pressure.

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