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Preparation and critical current density of hot pressed $Bi_2Sr_2Ca_2Cu_3O_x$/Ag tapes

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$Bi_2Sr_2Ca_2Cu_3O_x$(Bi-2223)/Ag tapes have been prepared by hot pressing performed at 800–840 °C for 12–96 h under 6 or 12 MPa in air. The highest transport critical current density, J_c, is 3900 A cm^{-2} at 77 K and 8800 A cm^{-2} at 65 K under zero magnetic field, which is observed in tape hot pressed at 820 °C under 12 MPa for 24 h twice. The tape has undergone a cold pressing under 260 MPa between hot pressings. J_c is limited to 120 A cm^{-2} in tape hot pressed for 48 h continuously, in spite of total hot pressing time, temperature and pressure all being the same as for tape hot pressed for 24 h twice. It is found that alternate hot pressing and cold pressing is effective in the preparation of Bi-2223 tapes with high J_c, which is determined by the strength of grain coupling. Grain coupling is strengthened in tape hot pressed with an intermediate cold pressing. © *1998 Chapman & Hall*

1. Introduction
At present, oxide superconducting tapes consist of sintered ceramics, as single crystals of sufficient size for application have not yet been prepared successfully. In order to obtain tapes with good superconducting properties, it is necessary to achieve good alignment and strong superconducting coupling between grains. Many methods for preparing superconducting tapes, especially $Bi_2Sr_2CaCu_2O_x$ (Bi-2212) and $Bi_2Sr_2Ca_2Cu_3O_x$ (Bi-2223) compounds, have been reported. For Bi-2212 compounds, the Ag-sheathed method (powder in tube method) [1–3] and the doctor-blade casting method on Ag sheets with partial melting [4] are advantageous for good alignment and strong coupling, and Bi-2212 tapes with high critical current density, J_c, have been obtained using these methods. On the other hand, the partial melting method has not yielded Bi-2223 tapes with J_c high enough for application at 77 K. Because Bi-2223 tapes are mainly prepared by repeating solid state sintering and cold pressing, it takes a long time (several tens of hours) to obtain tapes with high J_c. Hot pressing is considered useful in preparing highly densified and aligned tapes in a short time. Therefore it is expected that Bi-2223 tapes can be prepared in a shorter time by hot pressing than by sintering under 101 kPa. One of the main purposes of this study is to find out the optimal hot pressing conditions for the preparation of Bi-2223/Ag tapes. The relationship between superconducting properties and grain coupling is also discussed.

2. Experimental procedure
Bi-2223 powder with a composition of $Bi_{1.84}Pb_{0.34}Sr_{1.97}Ca_{1.97}Cu_{3.06}O_x$ was prepared under a low oxygen partial pressure [5]. The powder was suspended in an organic binder and deposited on an Ag sheet of 15 mm length, 5 mm width and 150 µm thickness. After evaporation of the organic binder (~140 °C), two such sheets were stuck together with their superconducting sides facing each other, wrapped in another Ag sheet (50 µm thickness), and pressed to densify under 260 MPa at room temperature (r.t.). The green tapes were heated at 500 °C for 3 h without additional pressure in order to eliminate the organic binder completely and hot pressed at 800–840 °C under 6 or 12 MPa for 24–96 h in air using an Al_2O_3 mould. MgO powder was used to avoid reaction between Ag and Al_2O_3. Intermediate cold pressing (260 MPa) was performed at room temperature every 24 h. Zero resistivity temperature, $T_{c,zero}$ and J_c were measured using a standard four-probe method. The J_c measurement was performed at 77–65 K under 0 (zero applied magnetic field) T using liquid N_2 and a rotary pump. The criterion for the determination of J_c was 1.0 µV cm^{-1}. X-ray diffraction (XRD) and electron probe micro analysis (EPMA) were employed to determine the impurity phases in the tapes. Microstructural observation was carried out using a scanning electron microscope (SEM). In order to estimate the strength of superconducting coupling at the grain boundaries, alternating current (a.c.) susceptibility measurement was carried out by means of a commercial superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion
3.1. Hot pressing conditions and superconducting properties
$T_{c,zero}$ and J_c at 77 K under 0 T for tapes hot pressed at 800–840 °C under 6 or 12 MPa for 24 h are listed in

TABLE I $T_{c,zero}$ and J_c at 77 K under 0 T for hot pressed Bi-2223 tapes

Hot pressing conditions (Hot pressing time: 24 h)		$T_{c,zero}$ (K)	J_c (A cm^{-2}) at 77 K 0 T
°C	MPa		
800	6	103.5	82
800	12	100.5	160
820	6	104.0	1200
820	12	107.0	2800
840	12	< 77.3	0

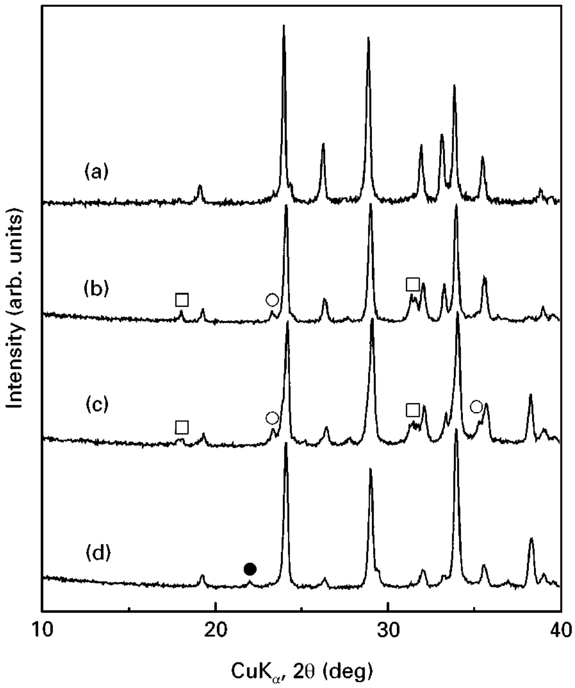

Figure 1 XRD patterns for Bi-2223 powder (a), and tapes hot pressed under 12 MPa for 24 h at 800 °C (b), 820 °C (c) and 840 °C (d). Peaks due to (○) Bi-2212, (●) Bi-2201, (□) Ca_2PbO_4.

Table I. Zero resistivity is observed at temperatures higher than 100 K for tapes hot pressed at 800 and 820 °C. The highest $T_{c,zero}$ is 107 K for tape hot pressed at 820 °C under 12 MPa. For tapes hot pressed at 800 °C, J_c is less than 200 A cm^{-2}. On the other hand, it is of the order of 10^3 A cm^{-2} for tapes hot pressed at 820 °C. J_c is higher for tapes hot pressed under 12 MPa than 6 MPa at both 800 and 820 °C. The highest J_c is 2800 A cm^{-2} for tapes hot pressed at 820 °C under 12 MPa. The intensities of the XRD peaks due to Ca_2PbO_4 are greater for tapes hot pressed at 800 °C than at 820 °C (Fig. 1). It is thought that the sintering rate of Bi-2223 powder is slower at 800 °C than 820 °C. Therefore a greater amount of Ca_2PbO_4, which is thought to be formed in the early stage of hot pressing, remains in tapes hot pressed at lower temperature. As a result, grain coupling is weaker and J_c lower in tapes hot pressed at 800 °C than at 820 °C. Although XRD peaks due to Bi-2212 and Ca_2PbO_4 are not observed, an XRD peak due to Bi-2201 is observed in tape hot pressed at 840 °C. Zero resistivity is not observed down to 77 K for tape hot

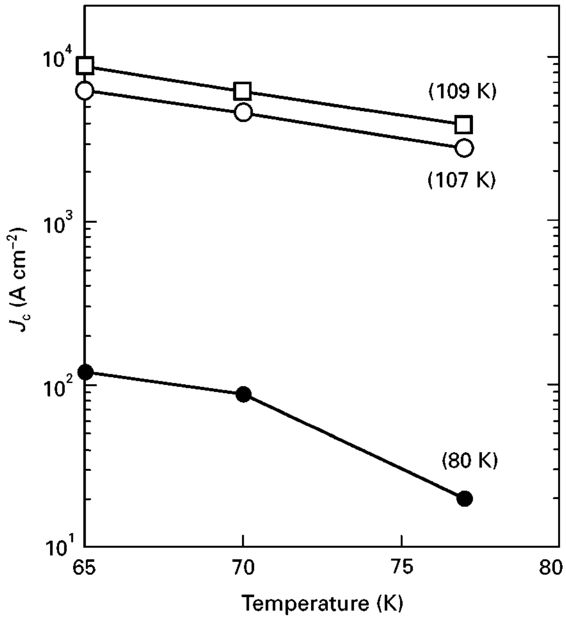

Figure 2 J_c under 0T for tapes hot pressed at 820 °C under 12 MPa for 24 h (○), 24 h twice (□) and 48 h continuously (●). $T_{c,zero}$ is shown in parentheses.

pressed at 840 °C. These results suggest that impurity phases are different between tapes hot pressed at 820 and 840 °C and that grain coupling is weaker in tape hot pressed at 840 °C than 820 °C. Yan *et al.* have reported that Bi-2201 and an amorphous phase are present at the grain boundaries of Bi-2223 tapes [6]. It is thought that, in tapes hot pressed at 840 °C, Bi-2201 and the amorphous phase are present at the grain boundaries. From the above results, it is concluded that a heating temperature of 820 °C and pressure of 12 MPa are close to the optimal conditions for hot pressing.

Fig. 2 indicates J_c at 77–65 K under 0 T for tapes hot pressed at 820 °C for 24 h once, twice with intermediate cold pressing, and for 48 h continuously. J_c and $T_{c,zero}$ are higher for tapes hot pressed for 24 h twice than once. It is clear that hot pressing for 24 h is not sufficient to achieve good superconducting properties. Although the total hot pressing time is the same as for tape hot pressed for 24 h twice, J_c and $T_{c,zero}$ are very low for tape hot pressed for 48 h continuously. In order to prepare Bi-2223 tapes with high J_c, tapes need to be hot pressed for 48 h at 820 °C under 12 MPa, although J_c and $T_{c,zero}$ are depressed in tape hot pressed for more than 24 h continuously. Intermediate pressing is needed to obtain high J_c in Bi-2223 tapes sintered under 101 kPa. The grains are highly aligned and density increases by the intermediate pressing. In consequence, grain coupling is strengthened and J_c increases. In order to achieve increases in J_c, a pressure of 10^2–10^3 MPa is needed at r.t. [2, 7]. Hot pressing is effective for high alignment and density [8]. However, because the pressure of hot pressing is limited up to several tens of MPa, the pressure is not enough for high alignment and density. Therefore alternate hot pressing and cold pressing is effective in the preparation of tapes with high J_c.

3.2. Number of hot pressings and superconducting properties

The effect of the number of hot pressings on J_c at 77 K under 0 T and $T_{c,zero}$ is illustrated in Fig. 3. The highest J_c and $T_{c,zero}$ are observed in tapes hot pressed at 820 °C for 24 h twice and are 3900 A cm^{-2} and 109 K, respectively. J_c increases with decreasing measurement temperature and reaches its highest value of 8800 A cm^{-2} at 65 K in tape hot pressed twice (Fig. 2). XRD patterns for these tapes are shown in Fig. 4. XRD peaks due to Bi-2212 are observed in all tapes. The intensities of XRD peaks due to Ca_2PdO_4 are greater in tapes hot pressed once than tapes hot pressed twice or three times. This result indicates that sintering of Bi-2223 powder progresses under repeated hot pressing. In tapes hot pressed four times, the intensities of XRD peaks due to Ca_2PbO_4 and Bi-2212 increase. This seems to be due to decomposition of the Bi-2223 phase. Fig. 5 shows back scattering images for these tapes. (Sr,Ca)–Cu–O grains assigned by EPMA are observed in tapes hot pressed three or four times. Although small grains of CuO are present, no (Sr,Ca)–Cu–O grains are observed in tapes hot pressed once or twice. The highest J_c is observed in tapes hot pressed twice with an intermediate cold pressing. However, hot pressing more than twice leads to the formation of large (Sr,Ca)–Cu–O grains and the depression of J_c. It is clear from a.c. susceptibility measurement that the strength of grain coupling is the origin of the change in J_c with the number of hot pressings.

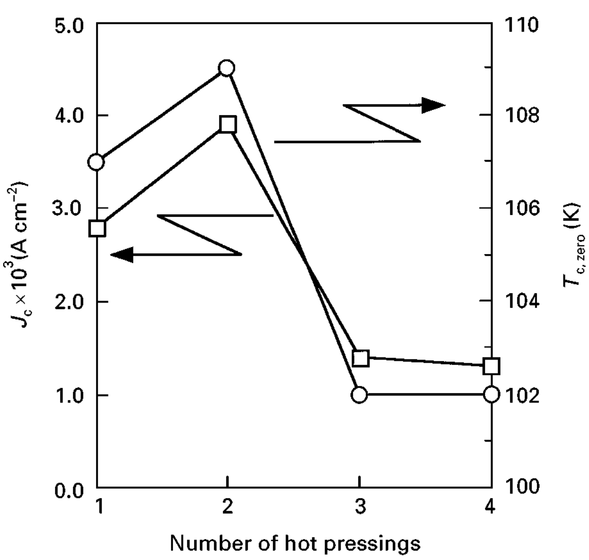

Figure 3 Dependence of J_c on number of hot pressings at 77 K under 0 T (□) and $T_{c,zero}$ (○) for tapes hot pressed at 820 °C under 12 MPa for 24 h once.

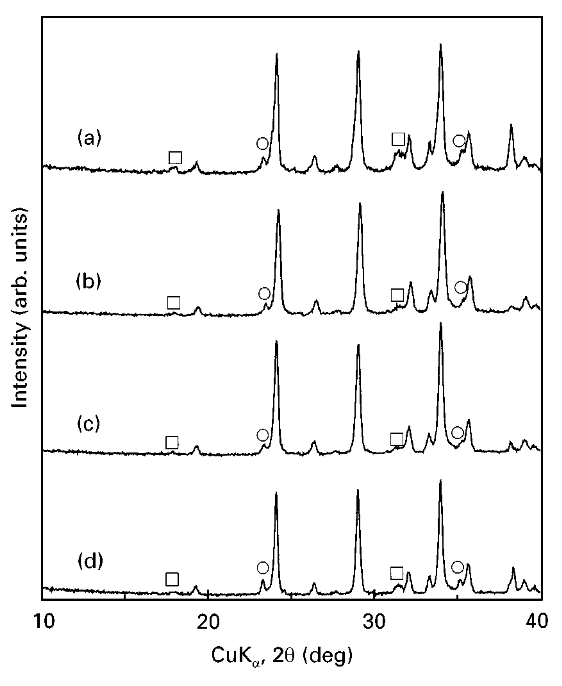

Figure 4 XRD patterns for tapes hot pressed at 820 °C under 12 MPa for 24 h once (a), twice (b), three times (c) and four times (d). (○) Bi-2212, (□) Ca_2PbO_4.

3.3. Strength of grain coupling

Fig. 6 shows the temperature dependence of the a.c. susceptibility measured under zero direct current (d.c.) field, amplitude, h, of 159 A m^{-1} and frequency, f, of 100 Hz. Temperature is normalized by the magnetic superconducting transition temperature $T_{c,mag}$, and a.c. susceptibility by χ' at 10 K. The peak temperature of χ'' and the width of the superconducting transition, ΔT_c, are plotted in Fig. 7. Here ΔT_c is evaluated from $T_{c,on} - T_{c,zero}$. $T_{c,on}$ corresponds to a temperature where the tangent lines for the resistivity-temperature curve above and below the transition actually cross each other. Large ΔT_c is observed in tapes including weakly coupled grain boundaries [9]. On the other hand, χ'' has a broad peak for each tape. Two peaks of χ'' are reported for the oxide superconducting ceramics [10, 11]. One is due to the penetration of the a.c. field into the grains and the other results from penetration into the grain boundaries. The latter appears generally at lower temperature, in broader form, and has a larger susceptibility value than the former. The χ'' value due to the penetration into the grains is sometimes too small to be observed. The peaks in Fig. 6 are due to the penetration of the a.c. field into the grain boundaries. The lower peak temperature corresponds to the larger influence of weak coupling at the grain boundaries. $T_{\chi''peak}$ decreases with increasing ΔT_c. It is found that the strongest coupling is achieved by hot pressing twice.

The normalized peak temperature of χ'' ($T_{\chi''peak}/T_{c,mag}$) decreases with increasing amplitude, h, and is highest in tapes hot pressed twice under all values of h (Fig. 8). The inset of Fig. 8 plots h against the ratio between peak temperatures and those under 8.0 A m^{-1} [$T_{\chi''peak}(h)/T_{\chi''peak}$ (8.0 A m^{-1})]. It is reported that the larger the decrease in this ratio, the weaker is the coupling and the lower is J_c [12, 13]. Therefore it is found that the tapes affected most seriously by weak coupling are tapes hot pressed four times, and the strongest coupling is achieved by hot pressing twice. The above results indicate that J_c for hot pressed tapes is determined by the strength of the grain coupling.

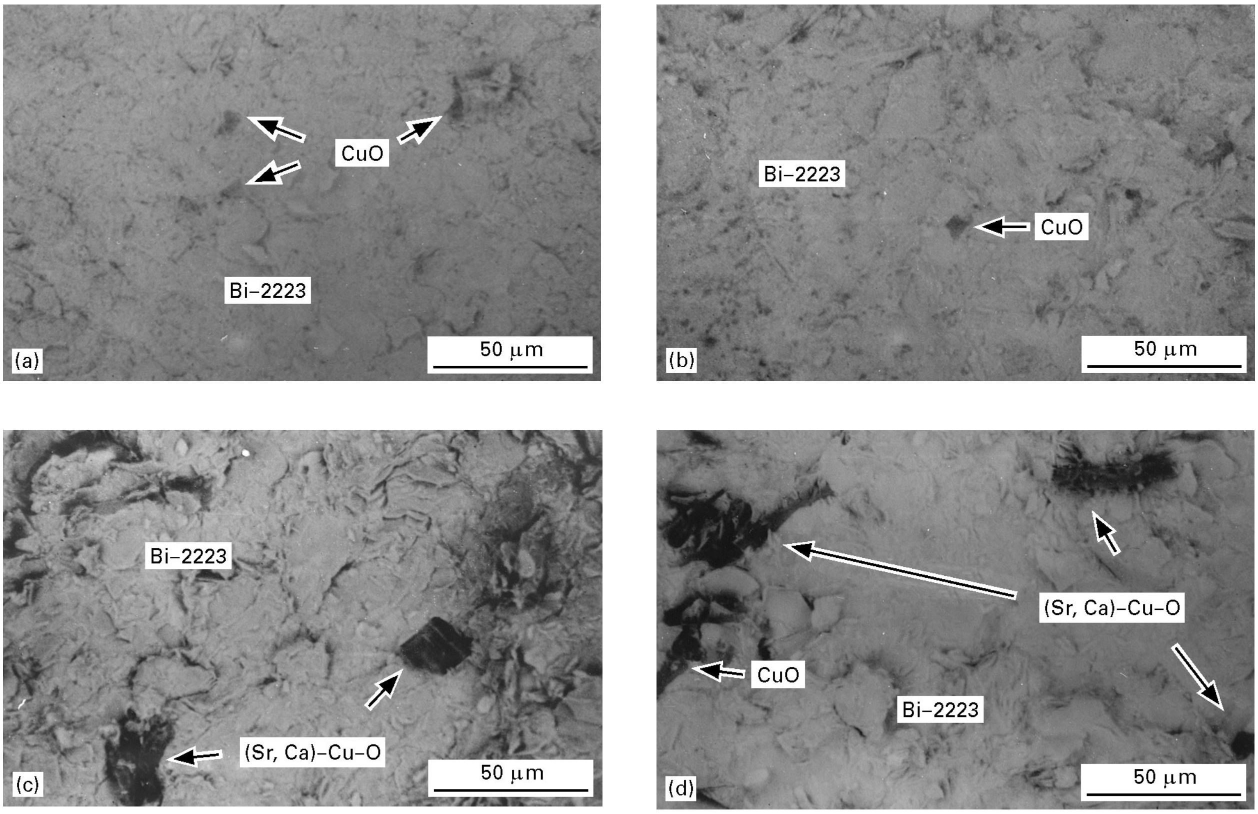

Figure 5 Back scattering images for tapes hot pressed at 820 °C under 12 MPa for 24 h once (a), twice (b), three times (c) and four times (d).

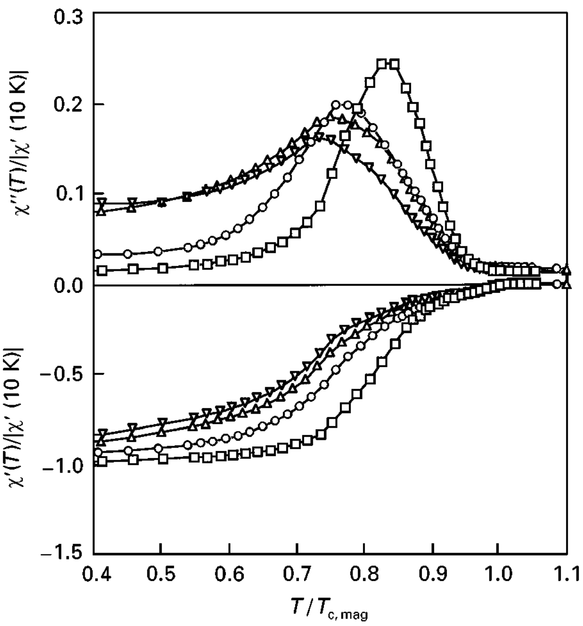

Figure 6 Temperature dependence of a.c. susceptibility for tapes hot pressed at 820 °C under 12 MPa for 24 h once (○), twice (□), three times (△) and four times (▽). Temperature is normalized by $T_{c,mag}$ and a.c. susceptibility by χ' at 10 K.

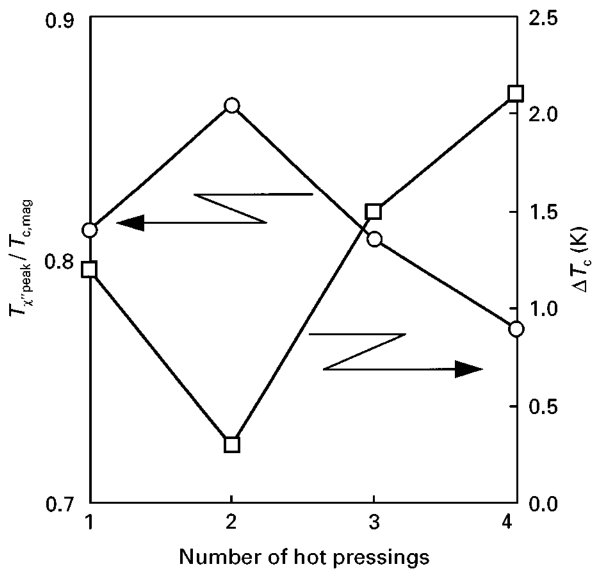

Figure 7 Dependence on number of hot pressings of normalized peak temperature of χ'', $T_{\chi''\mathrm{peak}}/T_{c,mag}$, (○) and width of superconducting transition, ΔT_c, (□).

A two-step transition is observed in the χ' curve for tapes hot pressed three or four times (Fig. 6). The onset temperature of the transition at lower temperature is 90–96 K for tapes hot pressed three or four times under $20\,\mathrm{A\,m^{-1}}$. This transition is not observed clearly in tapes hot pressed once or twice, as shown in Fig. 6. However, it appears under $0.50\,\mathrm{A\,m^{-1}}$. This transition results from the Bi-2212 phase [13]. The lower transition temperature is observed close to the peak temperature of χ''. This means that the Bi-2212 phase is present at the grain boundaries and that the χ'' peak results from the field penetration into the Bi-2212 phase. The Bi-2212 phase is formed by decomposition of Bi-2223 phase at the grain boundaries by hot pressing more than twice and weakens the grain coupling. The intensities of XRD peaks due to Bi-2212 and Ca_2PbO_4 in tapes hot presssed once are greater than in tapes hot pressed twice. Guo *et al.* have mentioned that the Bi-2223 phase is recovered from

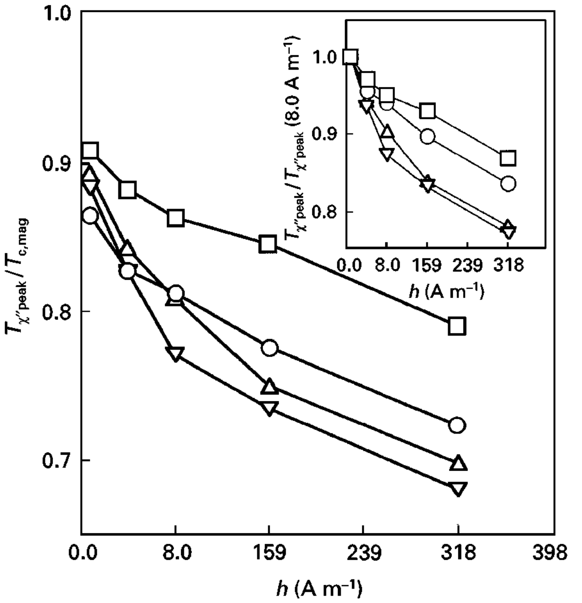

Figure 8 Amplitude dependence $T_{\chi''\mathrm{peak}}/T_{\mathrm{c,mag}}$. Inset: plot of h against the ratio between peak temperatures and those under $8.0\,\mathrm{A\,m^{-1}}$. The symbols correspond to tapes hot pressed at 820 °C under 12 MPa for 24 h once (○), twice (□), three times (△) and four times (▽).

the reaction of Bi-2212, Ca_2CuO_3 and CuO formed by decomposition during the partial melting process [14]. The Bi-2223 phase is recovered and the Bi-2212 phase decreases in the second hot pressing. In consequence, high J_c is achieved in tape hot pressed twice. The large (Sr,Ca)–Cu–O grains are observed in tapes hot pressed more than twice. Murayama and Sande have reported that Bi-2212 phase formed by hot pressing decomposes to (Sr,Ca)–Cu–O phases with large grain size in heat treatment of short duration, and that J_c increases due to decrease in the amount of Bi-2212 at the grain boundaries [15]. In the present study, on the other hand, the influence of the Bi-2212 phase at the grain boundaries becomes serious in tapes hot pressed three or four times, in spite of the formation of large (Sr,Ca)–Cu–O grains. The result indicates that the Bi-2223 phase decomposes to Bi-2212 and (Sr, Ca)–Cu–O phases. It is found from the a.c. susceptibility measurement that the amount of Bi-2212 at the grain boundaries increases with increasing (Sr,Ca)–Cu–O grain size and that the grain coupling becomes weak if hot pressing is repeated more than twice.

4. Conclusions

$Bi_2Sr_2Ca_2Cu_3O_x$ (Bi-2223)/Ag tapes have been prepared by hot pressing performed at 800–840 °C for 12–96 h under 6 or 12 MPa in air. The highest transport J_c is $3900\,\mathrm{A\,cm^{-2}}$ at 77 K and $8800\,\mathrm{A\,cm^{-2}}$ at 65 K under 0 T, observed in tape hot pressed at 820 °C under 12 MPa for 24 h twice. In order to achieve high J_c, the tapes need to be hot pressed for more than 24 h at 820 °C under 12 MPa, although J_c and $T_{c,\mathrm{zero}}$ are depressed in tape hot pressed for 48 h continuously. It is found that alternate hot pressing and cold pressing is effective in the preparation of tapes with high J_c. Grain coupling is stronger in tapes prepared by intermittent hot pressing than by continuous hot pressing, because high alignment of the grains and high density are achieved by cold pressing.

J_c is determined by the strength of grain coupling, which is strongest in tapes hot pressed at 820 °C for 24 h twice. The Bi-2212 phase at the grain boundaries weakens the superconducting coupling.

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