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Thermomechanical processing and transport current density of Ag-sheathed $(Tl,Cr)Sr_2(Ca_{0.9},Pr_{0.1})Cu_2O_7$ superconductor tapes

S.K. Chen, K.T. Lau, R. Abd-Shukor *

Department of Physics, School of Applied Physics, Universiti Kebangsaan Malaysia, 43600 Bangi Selangor D. E., Malaysia

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Abstract

Powders with nominal composition $(Tl,Cr_{0.15})Sr_2(Ca_{0.9},Pr_{0.1})Cu_2O_7$ (Tl-1212) and $T_c \sim 90$ K were used to fabricate Ag-sheathed superconducting tapes employing the powder-in-tube (PIT) method. The tapes were subjected to intermediate mechanical rolling or pressing. Conditions that enhance the transport critical current density (J_c) of the tapes were investigated. Optimum annealing temperature and period together with uniaxial pressing are necessary to increase J_c of the Tl-1212/Ag tapes. Annealing at 910 °C for 0.5–1 h enhanced the 1212 phase formation and improved intergranular connectivity between grains, as well as to provide healing for the fractured structure caused by deformation process. A relatively longer annealing time at higher temperature gave rise to secondary phases and resulted in the decrease of J_c. Mechanical uniaxial pressing greatly densified the tapes core and thus led to closer contact between grains. At liquid nitrogen temperature and zero field, J_c of the pressed tapes annealed at 910 °C for 1 h is 3060 ± 127 A cm^{-2}. The initial drastic drop of J_c in low fields (< 0.06 T) indicates the performance of the tapes is limited by weak links. No significant anisotropic transport properties were observed in applied magnetic field. This is due to the absence of texturing in the tapes as the grains are randomly oriented revealed through SEM micrographs. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tl-1212/Ag tapes; Phase formation; Intergranular connectivity; Weak links; Transport properties; Texturing

1. Introduction

The discovery of high-T_c superconductors has initiated tremendous efforts in developing the practical usage of the materials. Production of long length conductors with desirable transport properties is the issue of major concern for large scale applications. In the recent years, fabrication of Tl-based superconductor tapes by powder-in-tube (PIT) method has been reported [1–7]. One of the advantages in processing the Tl-based tapes is the relatively short annealing time compared with Bi-based tapes [4]. Up to date, reasonable J_c has been achieved in the Tl-based superconducting tapes exploiting various preparation conditions [1–7]. A flexible and long length scale Tl-1223 Ag-sheathed tape with $J_c \sim 10^4$ A cm^{-2} has also been successfully produced using the PIT method [8]. However, the tapes are still hindered by Josephson weak links and their applications in high magnetic field are strongly restricted. For liquid nitrogen level applications, both YBCO and BSCCO superconductors are limited by their weak links and weak pinning properties [9–11]. The high J_c in Bi-based tapes cannot be maintained at elevated temperatures and in applied fields due to their poor flux pinning characteristics. The reduction of J_c is even more drastic when the magnetic field is applied perpendicular to the tape surface.

The better in field behavior exhibited by single Tl–O layer systems such as Tl-1223 and Tl-1212 compared with multiple Tl–O layers superconductors provides alternative materials for high field and high current carrying applications. Single Tl–O layer materials are structurally similar to YBCO which has favorable pinning properties [12]. The relatively high irreversibility field of the materials is attributed to the better coupling of the adjacent Cu–O blocks along the *c*-axis [13] especially for Tl-1212 with the shortest insulating distance between the Cu–O superconducting planes

* Corresponding author. Tel.: +60-3-89292904; fax: +60-3-89293777.

E-mail address: ras@pkrisc.cc.ukm.my (R. Abd-Shukor).

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among all the Tl-based materials. Although the parent compound of Tl-1212 $TlSr_2CaCu_2O_7$ is difficult to synthesize in pure form, single or double substitutions could stabilise the phase formation and enhance T_c [14–16]. For double substitutions, a small amount of Pr content at the Ca site can lead to maximum pinning potential in $Tl_{0.5}Pb_{0.5}Sr_2Ca_{1-x}Pr_xCu_2O_y$ at $T > 30$ K [17]. The Cr-doped Tl-1212 materials which belong to single Tl–O families are of particular interest because they are easy to prepare and show high transition temperature [15,16]. The plate-like grains observed in the Cr-doped superconducting Tl-1212/Ag tapes may contribute to significant directional grain alignment [18]. Moreover, it was found that Tl-1212/Ag tapes give better pinning properties compared with Tl-1223 system in high magnetic field [19]. The Cr containing Tl-1212 thin film also showed excellent J_c in the order of 10^6 A cm^{-2} [20]. Therefore, Cr-doped Tl-1212 materials can be considered for the use in tape fabrication.

In this paper, we report the preparation conditions of doubly substituted Tl-1212 superconducting tapes with nominal composition of $(Tl,Cr_{0.15})Sr_2(Ca_{0.9},Pr_{0.1})Cu_2O_7$. Pr is substituted for Ca to stabilize the 1212 phase. The results from dc electrical resistance measurements, X-ray powder diffraction spectra (XRD) and the scanning electron micrographs (SEM) are presented. The variation of J_c with annealing temperature and time are shown. The transport properties of the tapes in magnetic fields applied parallel and perpendicular to the plane of the tapes are also discussed.

2. Tapes fabrication and experimental details

Superconducting powder with nominal composition $(Tl,Cr_{0.15})Sr_2(Ca_{0.9},Pr_{0.1})Cu_2O_7$ was prepared by two-step procedure using the solid state reaction method. A precursor was first made by mixing appropriate amounts of SrO, CaO, CuO and Pr_6O_{11} then ground for 1 h and subsequently calcined at 900 °C for 24 h with several intermittent grindings. Tl_2O_3 and Cr_2O_3 were then added into the reacted precursor. Excess Tl_2O_3 was used to compensate Tl loss due to the high volatility of Tl_2O_3 during annealing. The resultant compound was ground and pressed into pellet form of 13 mm in diameter and 2 mm thick. The pellets were annealed at 1000 °C for 5 min in O_2 flow atmosphere followed by furnace cooling.

The Tl-1212 pellets were then ground into fine powder before loading into a 40 mm long silver tube with outer and inner diameter of 6.0 and 4.5 mm, respectively. The initial packing density was 3.2 g cm^{-3}. The tube was closed at both ends with silver caps and successively drawn into wire of 1.0 mm in final outer diameter through a grooved roller. Superconductor tapes were made by deforming the wire from the initial diameter of 1.0 to 0.5 mm with rolling process, then heat-treated in flowing O_2 at 820 °C for 15 min and furnace cooled to room temperature. Since high J_cs were achieved in the just-rolled tapes [6,7], we fabricated one set of tapes by rolling as the only deformation mean. The tapes were further cold rolled to final thickness of 0.12 and 2.0 mm wide (just-rolled tapes). To examine the effect of pressing compared with rolling, a second set of tapes with 0.5 mm thick were directly pressed at 0.15 GPa resulting in 0.25 mm thick and 2.5 mm wide (pressed tapes). For characterisation, both the just-rolled and pressed tapes with small sections (3 cm each) were subjected to annealing temperature range of 845–910 °C for up to 2 h in O_2 flow atmosphere.

DC electrical resistance measurements were carried out with the standard four-probe method. The phase development in the pellets and tapes was characterized through XRD spectra using a Siemens D5000 diffractometer with Cu–Kα as radiation source. A Philips XL-30 scanning electron microscope (SEM) was used to record the microstructure of the samples. Transport critical current density (J_c) was determined by dc four-probe technique with the tapes immersed directly into liquid nitrogen. J_c measurements were performed on several tapes of the same mechanical heat treatment to confirm the reproducibility of the results. Electric field criterion of 1 μV cm^{-1} was used to define J_c. The transport current measurements were made in zero and applied magnetic fields up to 0.20 T. Magnetic fields were applied perpendicular to the direction of current flow, parallel ($B_{\parallel}$) and perpendicular ($B_{\perp}$) to the plane of the tapes.

3. Results and discussion

The dependence of electrical resistance on temperature of the pellet and the tape annealed at 910 °C for 30 min are shown in Fig. 1. A sharp transition was observed in the bulk sample with $T_c = 90$ K whilst the tape exhibited a lower value at 80 K. XRD analysis (Fig. 2) showed that the $(Tl,Cr_{0.15})Sr_2(Ca_{0.9},Pr_{0.1})Cu_2O_7$ (Tl-1212) phase is dominant. Table 1 lists the T_c obtained for the just-rolled and the pressed (marked with *) tapes prepared in this work. The T_c range from 80 to 90 K and never exceeded the zero transition temperature of the pellet sample. To evaluate the effect of annealing temperature on the transport J_c, the just-rolled tapes were annealed in the temperature range from 845 to 910 °C for 30 min. Fig. 3 shows the dependence of J_c on annealing temperature measured at 77 K and zero field. The J_cs of the tapes increased with annealing temperature. Results from XRD diffraction indicate that 1212 phase is the main phase in all the tapes. A minor phase of 1201 is observed in the tapes annealed at 845–890 °C and the amount decreased as the annealing temperature is increased. Fig. 4(a) shows the XRD pattern of the tapes annealed at 910 °C for 30 min with a dominant phase of 1212. From Fig. 5(a), SEM micrograph reveals the fractured grains structure in the tapes annealed at 845 °C. The fractured structure is probably resulted from the initial deformation through rolling process. For the tapes annealed at higher temperature as shown in Fig. 5(b and c), a melted-like instead of fractured structure was observed. At higher temperature, the relatively fast decomposition of Tl_2O_3 produced sufficient Tl_2O vapour that subsequently be able to establish connectivity between grains [21]. This shows that higher annealing temperature is crucial for fractured grains recovery and provide better intergranular connectivity between grains. Therefore, the increase in J_c with annealing temperature is associated with the enhancement in 1212 phase reformation and the improved links between grains.

As reported in previous studies [1–3,22], annealing time significantly affect the transport J_c of Tl-1223/Ag superconductor tapes. Thus, to optimise the annealing

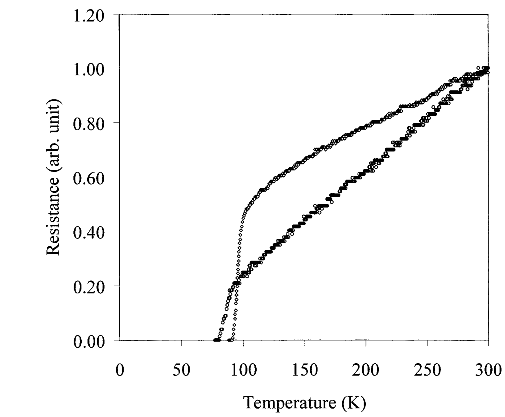

Fig. 1. The electrical resistance versus temperature curve for the pellet (◇) and a typical Ag-sheathed tape (○) of $(Tl,Cr_{0.15})Sr_2(Ca_{0.9},Pr_{0.1})Cu_2O_7$.

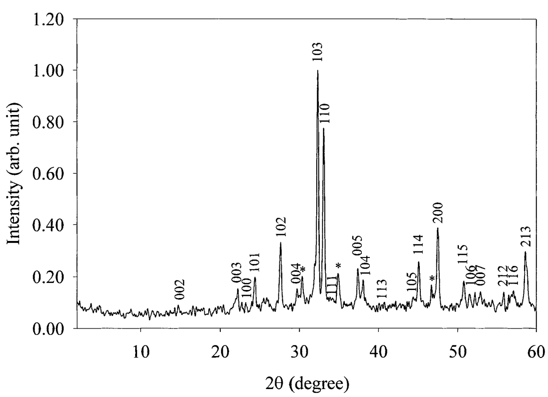

Fig. 2. X-ray powder diffraction pattern of the sample with nominal starting composition $(Tl,Cr_{0.15})Sr_2(Ca_{0.9},Pr_{0.1})Cu_2O_7$. (* corresponds to impurity).

Table 1
The measured T_c's of the just-rolled and the pressed (*) tapes annealed at various conditions

Annealing temperature (°C)	Annealing time (min)	T_c (K)
845	30	84
870	30	90
890	30	86
910	30	80
910	45	83
910	60	86
910	75	86
910	90	82
910	120	84
910*	60	84

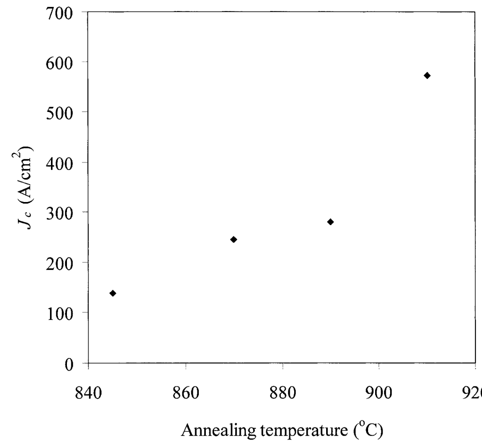

Fig. 3. J_c as a function of annealing temperature for the just-rolled tapes annealed for 30 min.

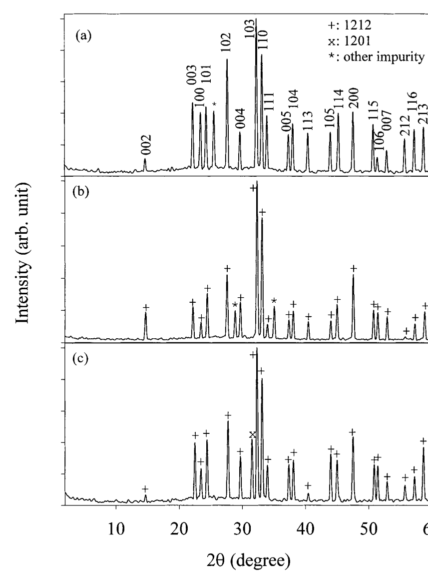

Fig. 4. The phase development of the just-rolled Tl-1212/Ag tapes annealed at 910 °C for (a) 30 min; (b) 1 h; and (c) the pressed tape annealed at 910 °C for 1 h.

conditions, the just-rolled tapes were annealed at 910 °C for duration up to 2 h. Fig. 6 shows J_c as a function of annealing time. The increase in J_c with annealing time below the peak value at 1 h is ascribed to the further improved connectivity between grains. The highest J_c was achieved in the tapes annealed for 1 h and then J_c decreased with longer annealing time.

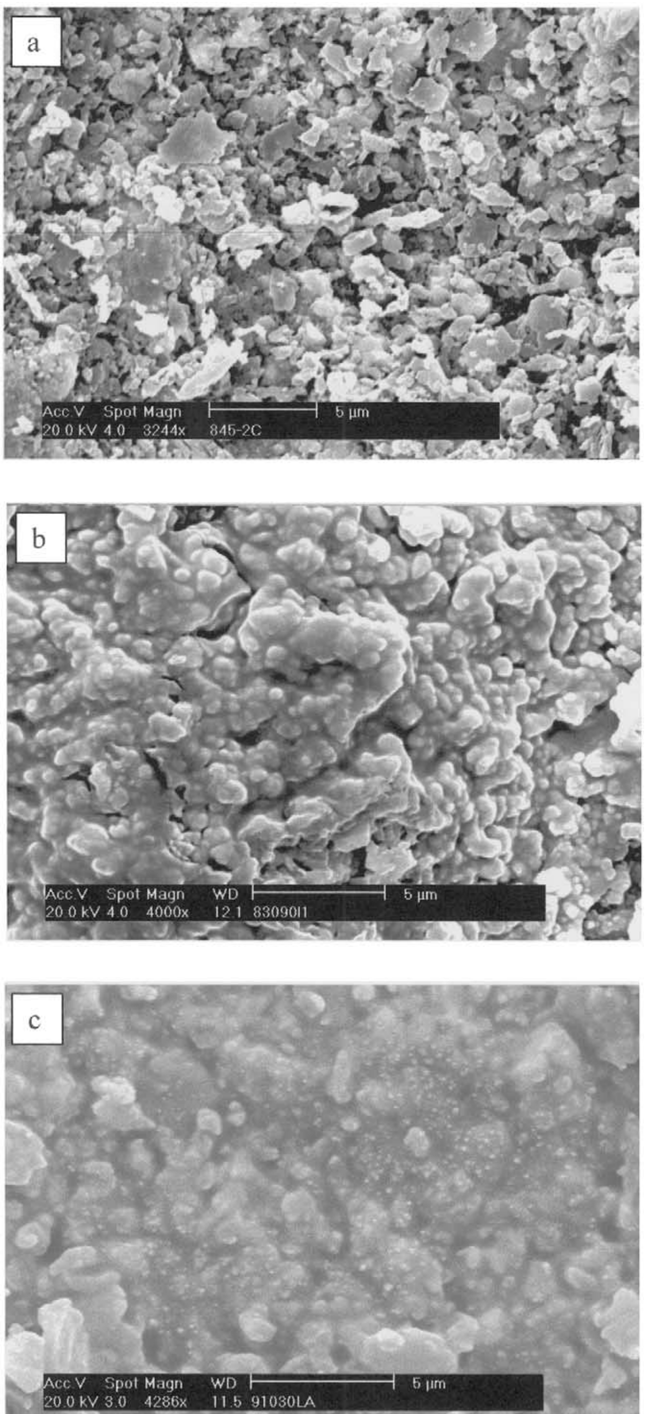

Fig. 5. Microstructural view of longitudinal section for the tapes annealed at (a) 845 °C; (b) 890 °C; and (c) 910 °C for 30 min.

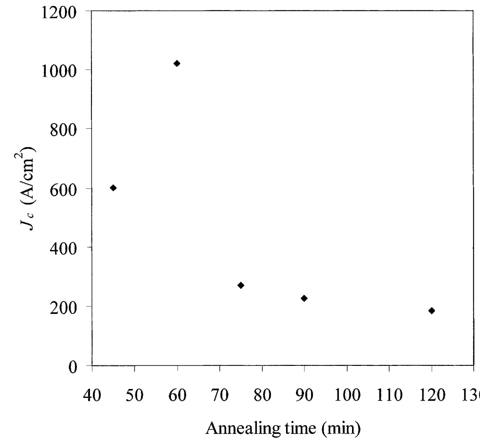

Fig. 6. Variation of J_c (77 K, $B=0$) with annealing time at 910 °C.

XRD patterns of the tapes indicate that 1212 phase is dominant with some impurity phases (Fig. 4b). In general, the amount of impurity phases decreased with longer annealing time. However, 1201 phase reappeared as minority phase in the tapes annealed beyond 75 min. Longer annealing time may cause severe Tl loss. Consequently, the change in the compositional stoichiometry reduced the 1212 phase formed in the tapes. From SEM images in Fig. 7, the tapes displayed irregular spherical grains and the intergranular connectivity is almost similar to those in Fig. 5(b and c). This suggests that the secondary phases consist of impurities and 1201 phase may act as obstacles which prevent the continuity of supercurrent path and resulted in J_c drop [23]. To further investigate the effect of pressing compared with just-rolled process on the transport J_c, the uniaxial pressed tapes with applied pressure load of 0.15 GPa were subjected to annealing at 910 °C for 1 h since this is the best annealing condition found for the just-rolled tapes. The pressed tapes showed highest J_c (3060 ± 127 A cm^{-2}) at $T = 77$ K and zero field despite the existence of minority 1201 phase (Fig. 4c). For the pressed tapes, the core is denser and the arrangement of the grains is closer to each other. Mechanical pressing forced the grains into closer contact and improved the intergranular connectivity [24]. By comparing the intensity of (00*l*)-peaks between the just-rolled and the pressed tapes, no signs of texturing is inferred. This result was further confirmed by the SEM micrographs in Fig. 7 showing the absence of texture induced either by rolling or pressing. For Bi-2223/Ag tapes, texturing and phase formation assisted by mechanical processing is critical in enhancing the transport J_c. Hence, the increased J_c in Tl-1212/Ag tapes is due to the densification of the tapes core similar to the Tl-1223/Ag tapes [1–3,24].

The dependence of J_c on thickness of the just-rolled tapes is shown in Fig. 8. The optimum annealing condition at 910 °C for 1 h was applied to the tapes with different thicknesses. Transport J_c at 77 K increased with decreasing thickness and reached the peak value at 0.12 mm. On the other hand, the Tl-1223 $(Tl_{0.5},Pb_{0.5})(Sr_{0.8},Ba_{0.2})_2Ca_2Cu_3O_y$ Ag-sheathed tape showed a maximum J_c at the thickness of 0.16 mm [25]. The increase in J_c with decreasing thickness is probably

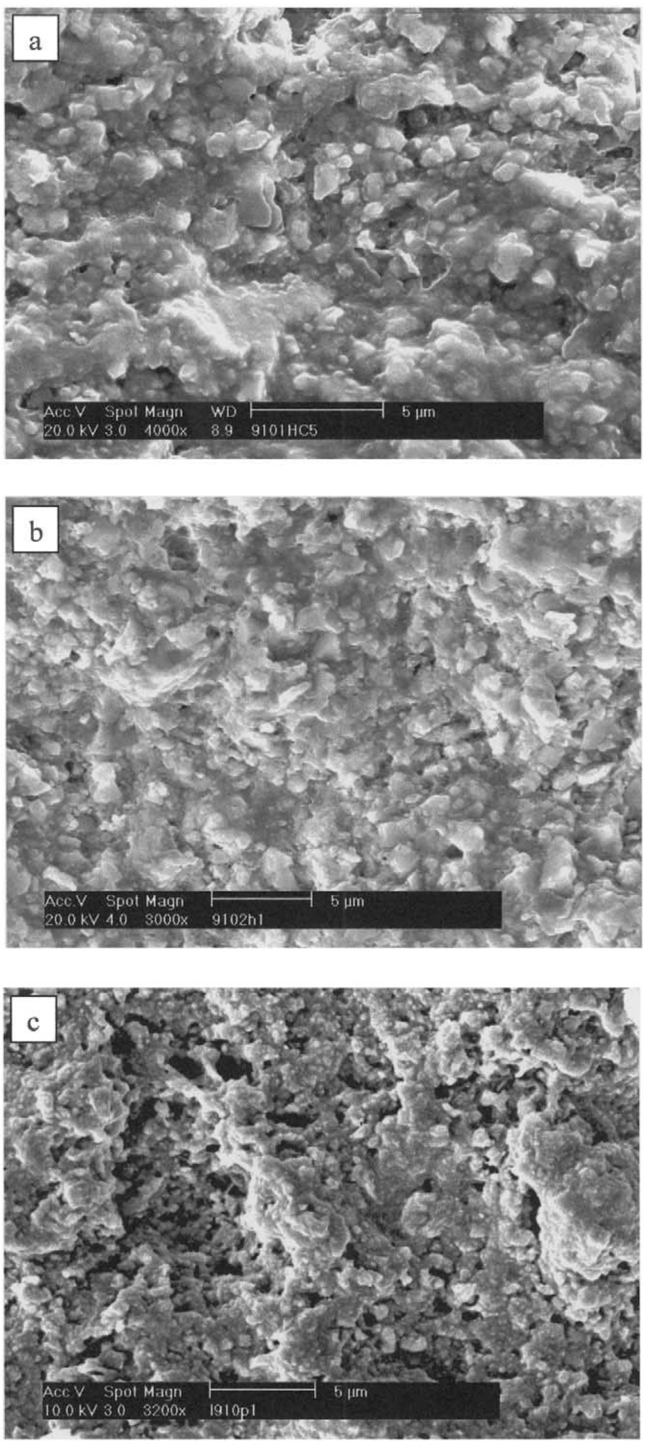

Fig. 7. Longitudinal sections of the just-rolled tapes annealed at 910 °C for (a) 1 h; (b) 2 h; and (c) the pressed tape annealed at 910 °C for 1 h.

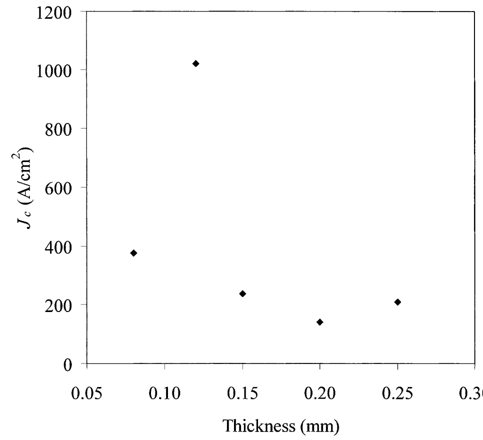

Fig. 8. The dependence of J_c at 77 K and zero field on the just-rolled tapes' thickness with annealing time of 1 h at 910 °C.

due to closer contact between grains as the core became denser. The tapes showed sudden increase in J_c up to thickness of 0.20 mm as reported in Y–Ba–Cu–O tape [26]. This implies that the densification of the tapes core become crucial in enhancing J_c for the tape thickness below 0.20 mm. However, further decrease in thickness below 0.12 mm resulted in the fall of J_c. It has been shown that J_c of PIT tapes is inversely proportional to the tape thickness until sausaging occurs [27]. Fig. 9 shows the existence of sausaging in the 0.08 mm thick tape in which the core uniformity was lost. This could be the reason for the decrease in J_c [22,27].

Fig. 10 shows the in field behavior of J_c up to 0.20 T for the just-rolled and pressed tapes. Magnetic field is applied perpendicular to the current flow direction and perpendicular or parallel to the tape plane. Both type of tapes exhibited weak links dominant because J_c dropped drastically in low magnetic field followed by a weaker field dependence for $B > 0.06$ T. The strong field dependence of J_c is similar to Tl-1223/Ag tapes. The plateau behavior of J_c is thought to be due to current flow through the remnant strongly linked percolative paths [4,5] after all of the weak links were decoupled by magnetic field.

The lack of strong anisotropic transport properties for the just-rolled and the pressed tapes is also seen from Fig. 10. The tapes did not exhibit any obvious anisotropic transport behavior with respect to the different directions of applied fields. As revealed from SEM micrographs (Fig. 7), irregular spherical grains were randomly distributed with no significant alignment in any direction. In Bi-2223/Ag tapes, the thin plate-like morphology grains are easier to align into preferred direction with mechanical working [28]. Conversely, the observed irregular spherical grains in the Tl-1212/Ag tapes may not be favourable for texturing [4–6,29]. The randomly distributed grains tend to form high angle grain boundaries in which the intergranular critical

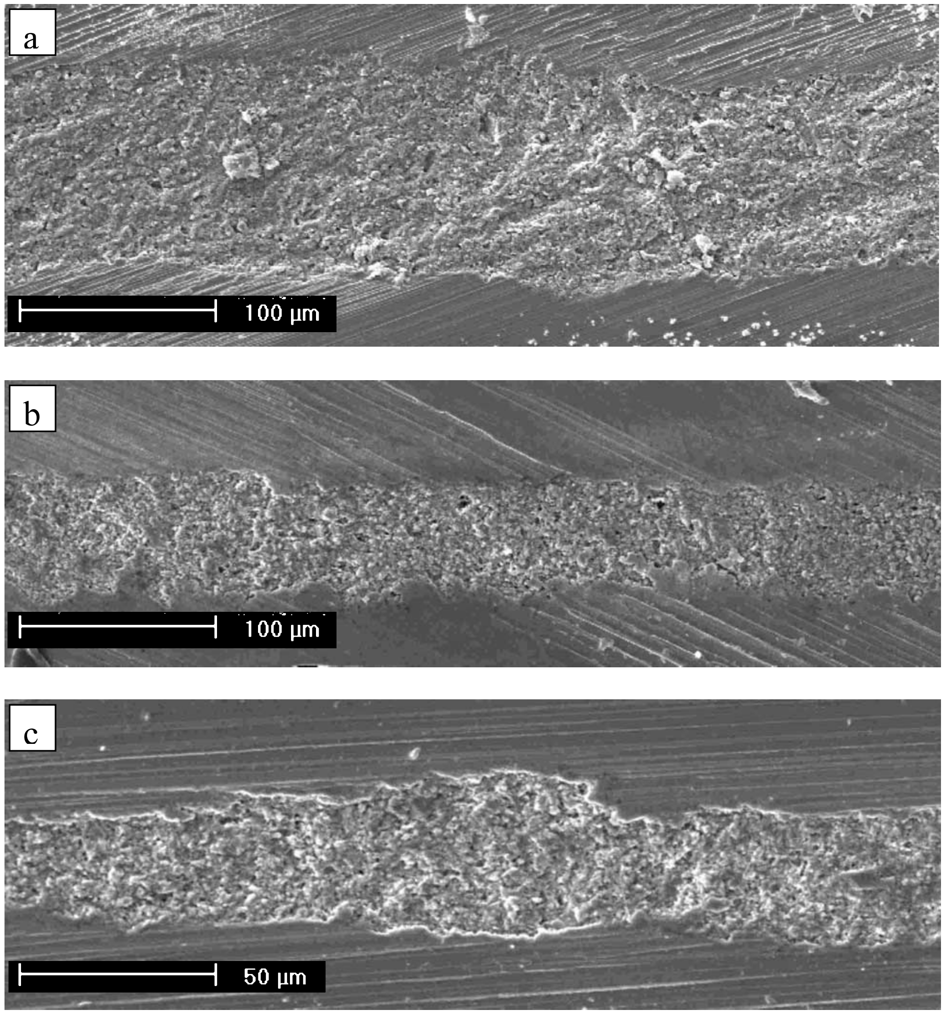

Fig. 9. Longitudinal SEM pictures of the just-rolled tapes (a) 0.20 mm; (b) 0.15 mm; and (c) 0.08 mm thick annealed at 910 °C for 1 h.

current is sensitive to the misorientation of adjacent grains [30–32]. Therefore, the low J_c in our Tl-1212/Ag tapes is attributed to the domination of weak links in most of the current path that arise from the randomly grains orientation.

4. Conclusions

The Tl-1212/Ag superconducting tapes have been fabricated and their transport current properties both in zero and applied magnetic fields were investigated. In order to increase the transport J_c, optimum conditions can be achieved by varying annealing temperature and time incorporating mechanical uniaxial pressing. The annealing conditions provide healing for the fractured structure caused by deformation process and improve grains connectivity, as well as in enhancing the formation of the 1212 phase. Relatively long annealing time at higher temperature gives rise to secondary phases and reduces 1212 phase. The secondary phases may resist supercurrent flow and consequently result in the J_c drop. Mechanical uniaxial pressing improves intergranular connectivity between grains by densifying the

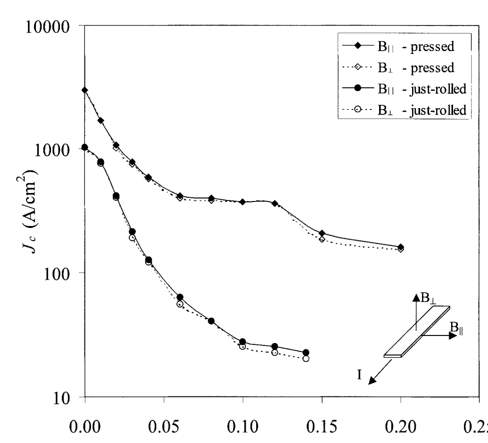

Fig. 10. Dependency of J_c on magnetic fields applied parallel ($B_{\|}$) and perpendicular ($B_{\perp}$) to the plane of the tapes.

tapes core and greatly enhances J_c. The drastic drop of J_c in low applied field ($B < 0.06$T) indicates that the Tl-1212/Ag tapes are dominated by weak links. The observed plateau behavior of J_c for $B > 0.06$ T is ascribed to the current flow through remnant strongly linked percolative paths in the tapes. No significant anisotropic transport properties were observed either in the just-rolled or the pressed tapes as J_c did not show any dependency on the different directions of applied fields. This is due to the absence of favourable texturing in the tapes as the grains are randomly oriented as revealed from SEM micrographs. The overall low J_c is attributed to the existence of weak links, which dominate the supercurrent path and the absence of significant texturing in the tapes. The lack of strong anisotropy in the transport critical current density for the Tl-1212/Ag tapes implies that they may have technological advantages over the large in field anisotropic J_c behavior of Bi-2223/Ag tapes. This is especially true for low J_c applications as described by Pavese et al. [33]. Moreover, J_c can be further increased by applying additional pressing load in order to densify the tapes core.

Acknowledgements

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