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Enhanced Densification in Tl-1223/Ag Tapes Prepared Using Pretreated Precursors

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전처리 precursor를 사용하여 제조한 Tl-1223/Ag 테이프에서의 향상된 치밀화

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Abstract

The effects of reacted precursors on phase evolution, microstructure, J_c and junctional characteristic of the inter-granular contacts were investigated in Ag-sheathed Tl-1223 tapes prepared using three kinds of reacted precursors, and compared to those in the tape prepared using an unreacted precursor. The precursors were prepared by heat-treating a mixture of Sr-Ba-Ca-Cu-O, Tl_2O_3, PbO and Bi_2O_3 powders at 805℃ (precursor Ⅰ), 840℃ (precursor Ⅱ) and 905℃(precursor Ⅲ) for 20 min. Tl-1223 phase content, grain size and J_c in the tapes appeared to increase in an order of precursors Ⅰ, Ⅱ and Ⅲ. Compared to tapes prepared using an unreacted precursor, the tapes prepared using precursors Ⅱ and Ⅲ revealed reduced pore and impurity densities and an enhanced texture. Also characteristic of inter-granular contacts and fraction of strong-links were improved. The improved properties are attributed to enhanced densification resulting from using the reacted precursors.

Keywords : Tl-1223/Ag tapes, directional grain-alignment, grain-connectivity, high J_c, powder-in-tube method

I. Introduction

Tl-1223 high-T_c superconductor has been known to be one of promising candidates for practical applications due to its relatively excellent pinning property, which is believed to originate from the relatively short distance between Cu-O layers, compared to those of other high T_c superconductors [1]. In contrast to remarkable advances [2-4] in obtaining high J_c in Tl-1223 coated conductors prepared using deposition techniques, the progress in Tl-1223 tapes prepared by means of the powder-in-tube (PIT) method, has been slowed down. The main obstacles in obtaining high J_c in Tl-1223 PIT tapes have been poor connectivity among Tl-1223 grains and little directional alignment of Tl-1223 grains in the tape core [1,5,6]. So, numerous

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attempts to overcome obstacles by finding optimal chemical compositions and/or optimal preparation methods have been conducted [5-20].

As a result of such efforts to find the optimal compositions, high J_c's up to 1.8×10^4 A/cm^2 at 77 K and under self-fields were obtained in just-rolled $Tl_{0.8}Pb_{0.2}Bi_{0.2}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_{9+\delta}$ tapes due to enhanced grain-connectivity resulting from using the composition [19]. Also high J_c's up to 2.5×10^4 A/cm^2 at 77 K and under self-fields were obtained in just-rolled $Tl_{0.8}Pb_{0.2}Bi_{0.2}Sr_{1.8}Ba_{0.2}Ca_{2.2}Cu_3O_{9+\delta}$ tapes, due to enhanced directional-grain-alignment and core density, which were believed to result from enhanced flatness of Tl-1223 grains originating from the composition used and from incorporation of an intermediate rolling during heat-treatment [20]. However, the field dependence of J_c's in both tapes revealed that the J_c's were still governed by significant weak-links [21]. Also the microstructure analysis revealed that the core densities of both tapes were still lower than the desired one for the practical applications and Tl-1223 grains were poorly connected in a sense of grain-linking [21]. Therefore, the microstructure needs to be further improved for the practical applications.

Unlike relatively successful results in finding an optimum chemical composition, many efforts to find optimum preparation methods not been successful. Accordingly, not much information on the optimum preparation methods has been available. Only noticeable was the work of Selvamanickam et al. [11] on the effects of phase content in precursors on J_c. They prepared Tl-1223/Ag tapes by using three different precursors, which were an unreacted precursor consisted of a mixture of Sr-Ba-Ca-Cu-O, Tl_2O_3 and Bi_2O_3 (or PbO) powders, and two types of reacted precursors containing Tl-1212 and Tl-1223 phase, respectively, as a main phase. They found that the unreacted precursor resulted in the highest J_c and the precursor mainly containing Tl-1212 the lowest J_c. Even though they did not clearly explain the cause of the precursor dependence of J_c, they claimed that the unreacted precursor would be more beneficial in healing out the cracks occurred during the intermediate mechanical working than the reacted one, and hence resulting in higher J_c. They also insisted that using the unreacted powder would offer other benefits such as reduced processing time, easy thallination and mitigated formation of sausages during mechanical working.

Based on earlier works of the present authors on Tl-1223 tape preparation [18-23], however, it is intuitively believed that the tapes prepared using the unreacted precursor can never circumvent the disadvantages resulting from the virginity in a chemical reaction point of view, such as lower density, severe volume expansion due to Tl evaporation, and from various shapes of constituent particles of the unreacted precursor. Inversely, it is likely that using reacted precursors get benefits such as reduced vapor pressure of volatile elements, higher density and plate-like constituent particles of the reacted precursors, and result in a denser and more textured microstructure, and thus high J_c, provided that the phase content of the reacted precursor and the detailed preparation process are properly controlled in order to fully heal out the cracks and not to generate the severe sausages.

The present study was performed to search an optimal state of the reacted precursor and an optimal preparation process for the desired microstructure and thus high J_c. Three kinds of reacted precursors with $Tl_{0.8}Pb_{0.2}Bi_{0.2}Sr_{1.8}Ba_{0.2}Ca_{2.2}Cu_3O_{9+\delta}$ nominal composition were prepared and then used for Tl-1223 tape preparation. Phase evolution, interface uniformity, microstructure, J_c and junctional characteristic of the inter-granular contacts in the tapes prepared using various thermo-mechanical treatment were investigated, and compared to those in the tape prepared using an unreacted precursor.

II. Experimental

Three kinds of precursors of $Tl_{0.8}Pb_{0.2}Bi_{0.2}Sr_{1.8}Ba_{0.2}Ca_{2.2}Cu_3O_{9+\delta}$ nominal compositions were prepared as follows:

To prepare the prepowder Sr-Ba-Ca-Cu-O, $SrCO_3$, $BaCO_3$, $CaCO_3$ and CuO powders were mixed in its stoichiometric ratio, heat-treated at 920℃ for 48 h with intermediate grindings per 24 h. The prepowder was ground and heat-treated at 700℃ for 3 h in vacuum ($<10^{-5}$ Torr), and reground. Then the prepowder was mixed with Tl_2O_3, PbO and Bi_2O_3

powders according to their stoichiometric ratios, heat-treated at 805 (precursor Ⅰ), 840 (precursor Ⅱ) and 905℃ (precursor Ⅲ), respectively, for 20 min, quenched to room, and then reground. 805℃ was chosen because it is expected that the material at the temperature is free of Tl-1223 phase and mostly composed of Tl-1212. 840 and 905℃ were chosen because they have been identified optimum temperatures resulting in the highest fraction of Tl-1223 in tapes and pellets, respectively, of the present composition in our previous study [19,20,22]. The heat-treatment time of 20 min was chosen because heat-treating a pellet of the present composition at 905℃ just for 1 h resulted in prominent Tl-1223 peaks in XRD pattern in our previous study [22].

Then Ag-sheathed Tl-1223 tapes were prepared by using the three precursors mentioned above. The tapes were prepared using the powder-in-tube method as follows:

Three different precursors were filled into Ag-tubes 10 mm O.D. and 8 mm I.D., respectively. The tubes were drawn to wires ~1.29 mm in diameter using a 15% reduction rate and a 2.7 cm/sec drawing speed, rolled to tapes 0.216 or 0.126 mm thick using a 15% reduction rate and a 1.2 cm/sec rolling speed. Then the tapes with two different thickness were heat-treated with an intermediate rolling, as follows: The 0.216 mm-thick tapes were heat-treated at 840℃ for 3~7 h, rolled to 0.115 mm thickness, and heat-treated at 840℃ for 4~7 h. On the other hand, the 0.126 mm-thick tapes were heat-treated at 840℃ for 3~7 h, rolled to 0.105 mm thickness, and heat-treated at 840℃ for 4~7 h. Further details on preparation of the tapes were shown elsewhere [18-23]. The latter thermo-mechanical treatment is very similar to that used to prepare tapes with high J_c's by using an unreacted precursor [20].

Relative molar ratios of constituent elements in the precursors were measured by using a Thermo Jarrell Ash model IRIS ion-coupled plasma (ICP) atomic emission spectrometer. The ratios were calculated based on 1.8 of relative molar ratio of Sr, as the least change in weight with heat-treatment for the precursor preparation was observed in Sr in the ICP analysis. Transport I_c's of the tapes were evaluated using dc 4-probe electrical measurements after immersing them into liquid nitrogen. Typical length of the tapes was 4~5 cm. I_c's were measured at the central part of the tapes. The distances between voltage taps and between current taps were 1 and 2 cm, respectively. A criterion of 1 μV/cm was used for I_c evaluation. J_c's were calculated from the measured I_c's under an assumption that 25% of the tape cross-section is the superconducting core, due to the occurrence of relatively severe sausages in the present study. The field dependence of transport I_c was measured at fields up to 0.8 T applied perpendicular to the tape surface. The field was applied using a LakeShore EM4-HV electromagnet. The phases present in the tape cores were investigated using a Philips PW 1710 x-ray diffractometer (XRD) using a Cu Kα target. The XRD measurements were performed after pealing off the Ag-sheath on one side using a blade. The microstructures of the tapes were examined on polished longitudinal cross-sections of the tapes using a Hitachi S-2700 scanning electron microscope (SEM) with an accelerating voltage of 20 kV. Inter-granular J_c's and characteristics were evaluated by measuring ac susceptibilities using a LakeShore 7000 ac susceptometer. Ac fields of 0.1~19 Oe in magnitude and of 1 kHz in frequency were applied parallel to the tape surface.

III. Experimental Results

3.1 Identification of compositions and phases of precursors

Table 1 shows weight percentages and relative molar ratios of constituent elements in precursors Ⅰ, Ⅱ and Ⅲ measured using the ion-coupled plasma analysis. It shows that loss of all the constituent elements increased with increasing heat-treatment temperature due to their evaporation at high temperatures. Significant losses due to the heat-treatments occurred in Tl, Pb and Bi. Their losses amounted up to 20% of their original contents. By the way, their molar ratios appeared to be higher in precursor Ⅲ than in precursors Ⅰ and Ⅱ. It may suggest that evaporation of other elements besides them is also significant at 905℃. Also total

Table 1. The weight percentage and the relative molar ratios of constituent elements in precursors Ⅰ, Ⅱ and Ⅲ measured using an ion-coupled plasma analysis. The ratios were calculated based on 1.8 of relative molar ratio of Sr.

Precursor used	Unit	Tl	Pb	Bi	Sr	Ba	Ca	Cu	Total wt.%
Ⅰ	wt.%	17.22	4.20	4.34	19.51	3.38	10.86	22.90	82.42
	mole ratio	0.68	0.16	0.17	1.80	0.20	2.19	2.91	
Ⅱ	wt.%	17.07	4.04	4.14	19.47	3.38	10.61	22.83	81.54
	mole ratio	0.68	0.16	0.16	1.80	0.20	2.14	2.91	
Ⅲ	wt.%	16.74	3.82	3.96	18.06	3.11	9.79	21.18	79.67
	mole ratio	0.72	0.16	0.17	1.80	0.20	2.13	2.91	

weight percentage decreased with increasing heat-treatment temperature. This phenomenon may reflect that the precursors intake a larger amount of oxygen with increasing heat-treatment temperature.

Fig. 1 shows XRD patterns taken from precursors Ⅰ, Ⅱ and. Ⅲ It shows that all the precursors contain Tl-1212 as a major phase, and Tl-1223, Tl-1201, $(Sr,Ca)_{14}Cu_{24}O_x$, $(Sr,Ba)PbO_3$, $(Sr,Ca)_2CuO_3$ and unreacted $CaCO_3$ as minor phases, indicating that they are consisted of almost the same phases. It is noted, however, that a significant difference among

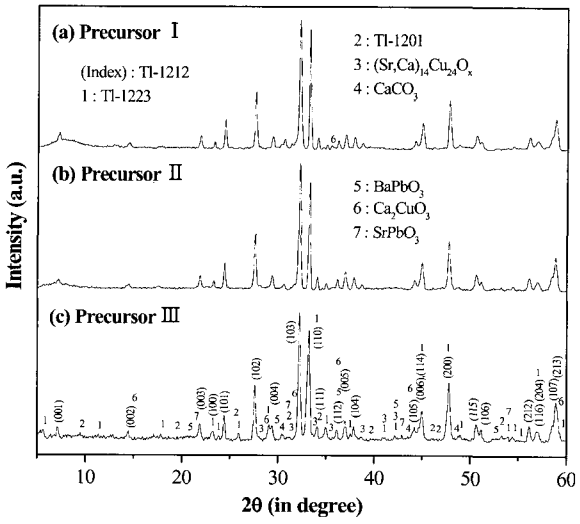


Fig. 1. XRD patterns taken on precursors (a) Ⅰ, (b) Ⅱ and (c) Ⅲ, which were prepared by heat-treating a mixture of Sr-Ba-Ca-Cu-O, Tl_2O_3, PbO and Bi_2O_3 powders at 805, 840, 905℃, respectively, for 20 min, quenching to room temperature and then grinding finely.

the precursors lies in the relative content of Tl-1223 phase. While precursors and Ⅰ Ⅱ contain little Tl-1223, precursor Ⅲ contains noticeable amount of Tl-1223.

3.2 Measurement of transport Jc

Tables 2 to 5 show tape preparation histories, dimensions and I_c's and J_c's at 77 K and in self-fields of tapes prepared using three different precursors. They reveal the dependence of J_c on precursor, degree of mechanical working and thermo -mechanical treatment history.

Tables 2 and 3 were taken in tapes rolled to 0.216 and 0.126-mm thickness, respectively, and heat-treated at 840℃ for 3~7 h, showing the dependence of J_c on precursor and heat-treatment time in tapes before intermediate rolling is applied. Both tables reveal that precursor Ⅲ resulted in the highest J_c, regardless of tape thickness. Also the tables show that J_c's are much higher in the thin tapes, i.e. the tapes more heavily worked before the heat-treatment, which are listed in Table 3, than in the thick ones, i.e. the less heavily worked ones, which are listed in Table 2. The optimal heat-treatment time for high J_c appeared to become shorter as the tapes were more heavily worked. However, J_c's shown in Table 3 are much lower than those in tapes prepared without intermediate rolling using an unreacted precursor, which were over 15,000 A/cm^2 at 77 K and under self-fields [19].

Table 4 was taken in tapes rolled to 0.216-mm thickness, heat-treated at 840℃ up to 7 h, rolled to 0.115-mm thickness, and then heat-treated up to 7 h. Table 5 was taken in tapes rolled to 0.126-mm thick-

Table 2. Preparation histories, dimensions and I_c's and J_c's at 77 K and in self-fields of tapes filled with precursors Ⅰ, Ⅱ and Ⅲ, rolled to 0.216 mm thickness and heat-treated at 840℃ for 3～7h, showing the dependence of I_c on precursor and heat-treatment time.

Precursor Used	Heat -treatment	Thick -ness (mm)	Width (mm)	I_c (A)	J_c (A/cm^2)
Ⅰ	840℃/3hr	0.242	3.00	2.216	1,220
	840℃/4hr	0.247	2.98	1.547	840
	840℃/5hr	0.241	2.97	2.077	1,160
	840℃/7hr	0.244	2.96	1.196	660
Ⅱ	840℃/3hr	0.263	2.98	3.137	1,600
	840℃/4hr	0.264	3.02	1.664	830
	840℃/5hr	0.277	3.05	2.577	1,220
	840℃/7hr	0.277	3.02	1.568	750
Ⅲ	840℃/3hr	0.246	3.04	5.177	2,770
	840℃/4hr	0.245	3.00	2.657	1,450
	840℃/5hr	0.249	2.98	4.109	2,220
	840℃/7hr	0.241	3.01	10.147	5,600

Table 3. Preparation histories, dimensions and I_c's and J_c's at 77 K and in self-fields of tapes filled with precursors Ⅰ, Ⅱ and Ⅲ, rolled to 0.126 mm thickness and heat-treated at 840℃ for 3～7h, showing the dependence of I_c on precursor and heat-treatment time.

Precursor used	Heat -treatment	Thick -ness	Width (mm)	I_c (A)	J_c (A/cm^2)
Ⅰ	840℃/3hr	0.148	3.59	3.948	2,970
	840℃/4hr	0.140	3.56	3.527	2,830
	840℃/5hr	0.142	3.64	3.032	2,350
	840℃/7hr	0.147	3.52	3.392	2,620
Ⅱ	840℃/3hr	0.148	3.50	4.433	3,420
	840℃/4hr	0.150	3.62	5.407	3,980
	840℃/5hr	0.148	3.56	5.038	3,820
	840℃/7hr	0.152	3.59	4.520	3,310
Ⅲ	840℃/3hr	0.148	3.63	12.561	9,350
	840℃/4hr	0.145	3.53	11.592	9,060
	840℃/5hr	0.147	3.56	9.788	7,480
	840℃/7hr	0.150	3.61	10.838	8,010

Table 4. Preparation histories, dimensions and I_c's and J_c's at 77 K and in self-fields of tapes filled with precursors Ⅰ, Ⅱ and Ⅲ, rolled to 0.216 mm thickness, heat-treated at 840℃ for 3～7h, rolled to 0.115 mm thickness, and heat-treated for 4～7 h again, showing the dependence of I_c on precursor and duration time of the first and the second heat-treatment (HT).

Precur -sor used	1st HT	2nd HT	Thick -ness (mm)	I_c (A)	J_c (A/cm^2)
Ⅰ	840℃/3hr	840℃/4hr	0.118	11.473	10,480
		840℃/5hr	0.119	16.121	14,730
	840℃/4hr	840℃/4hr	0.116	15.132	14,220
		840℃/5hr	0.117	15.275	14,270
	840℃/5hr	840℃/5hr	0.119	17.282	15,050
	840℃/7hr	840℃/7hr	0.119	11.458	10,030
Ⅱ	840℃/3hr	840℃/4hr	0.118	18.638	16,500
		840℃/5hr	0.113	19.827	18,670
	840℃/4hr	840℃/4hr	0.119	16.015	14,790
		840℃/5hr	0.120	21.009	18,280
	840℃/5hr	840℃/5hr	0.115	20.800	18,840
	840℃/7hr	840℃/7hr	0.112	13.414	12,980
Ⅲ	840℃/3hr	840℃/4hr	0.122	18.480	16,290
		840℃/5hr	0.116	19.212	18,400
	840℃/4hr	840℃/4hr	0.116	17.162	15,870
		840℃/5hr	0.111	21.906	21,450
	840℃/5hr	840℃/5hr	0.117	17.161	15,320
	840℃/7hr	840℃/7hr	0.112	13.698	13,220

ness, heat-treated at 840℃ up to 7 h, rolled to 0.105-mm thickness, and then heat-treated up to 7 h. In both tables, the J_c value appeared high in an order of precursors Ⅰ, Ⅱ and Ⅲ, regardless of degree of mechanical working. By comparing Table 4 to Table 5, it is recognized that when the tapes were heat-treated with an intermediate rolling, the tapes more heavily worked prior to the heat-treatment resulted in much lower J_c's. This result is contrary to that shown in Tables 2 and 3, which were obtained before the intermediate rolling applied. Another feature worthwhile to note is that in tapes prepared using precursors Ⅱ and Ⅲ, total heat-treatment time resulting in high J_c appeared to be shorter in tapes worked more heavily before the first heat-treatment. While the tapes rolled to 0.216-mm

thickness revealed high J_c's after total heat-treatment of 9~10h, the tapes rolled to 0.126 mm did after 7~8h. This difference may indicate that optimum heat-treatment time differs depending on degree of mechanical working applied during the preparation. In the present study, the highest J_c of 21,450 A/cm^2 was obtained in a tape rolled to 0.216-mm thickness, heat-treated at 840℃ for 4 h, rolled to 0.115-mm thickness, and then heat-treated for 5 h.

Table 5. Preparation histories, dimensions and I_c's and J_c's at 77 K and in self-fields of tapes filled with precursors Ⅰ, Ⅱ and Ⅲ, rolled to 0.126 mm thickness, heat-treated at 840℃ for 3~7 h, rolled to 0.105 mm thickness, and heat-treated for 4~7 h again, showing the dependence of I_c on precursor and duration time of the first and the second heat-treatment (HT).

Precursor Used	1st HT	2nd HT	Thick -ness (mm)	I_c (A)	J_c (A/cm^2)
Ⅰ	840℃ /3hr	840℃/4hr	0.113	4.709	4,460
		840℃/5hr	0.107	5.712	5,650
	840℃ /4hr	840℃/4hr	0.109	5.155	5,090
		840℃/5hr	0.107	5.044	5,150
	840℃ /5hr	840℃/5hr	0.110	5.102	4,800
	840℃ /7hr	840℃/7hr	0.110	5.638	5,600
Ⅱ	840℃ /3hr	840℃/4hr	0.119	9.963	8,720
		840℃/5hr	0.111	10.458	9,940
	840℃ /4hr	840℃/4hr	0.110	6.901	7,070
		840℃/5hr	0.111	8.504	8,330
	840℃ /5hr	840℃/5hr	0.108	6.628	6,530
	840℃ /7hr	840℃/7hr	0.109	6.353	6,370
Ⅲ	840℃ /3hr	840℃/4hr	0.109	11.223	11,010
		840℃/5hr	0.113	7.563	7,200
	840℃ /4hr	840℃/4hr	0.113	9.377	8,920
		840℃/5hr	0.108	8.235	8,090
	840℃ /5hr	840℃/5hr	0.111	7.996	7,730
	840℃ /7hr	840℃/7hr	0.113	7.594	7,230

3.3 X-ray diffraction analysis

Fig. 2 shows the change of XRD patterns with precursor in tapes prepared using three different precursors. The tapes were rolled to 0.126-mm thickness and heat-treated at 840℃ for 5 h. The figure shows that the tapes are composed of Tl-1223 as a main phase and Tl-1212, Tl-1201, $(Sr,Ca)_{14}Cu_{24}Ox$, and $BaPbO_3$ as minor phases. By the way, it is noted in the figure that depending on precursor, there exists a significant difference in relative intensities of Tl-1212 peaks, especially in (103) peak near $2\theta = 32.4°$, and of impurity peaks to the (110)(114) peak of Tl-1223 phase. The intensities of secondary phase peaks appeared to decrease in precursors Ⅰ, Ⅱ and Ⅲ turn. In the present study, precursor Ⅲ always resulted in least intense Tl-1212 and secondary phase peaks, when the tapes prepared using same preparation processes were compared. Under the present experimental regime, as it is believed that smaller content of Tl-1212 and secondary phases reflects larger content of Tl-1223 phase, higher J_c's in tapes prepared using precursor Ⅲ may be attributed to originated from higher content of Tl-1223 phase. Therefore, the presence of smallest content of Tl-1212 and secondary phases in tapes prepared using precursor Ⅲ may imply that the presence of very small amount of Tl-1223 phase in the precursor is beneficial to get a high volume

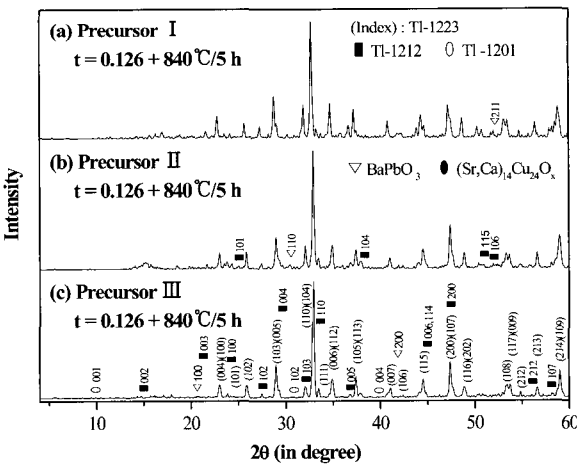


Fig. 2. XRD patterns taken on tapes filled with precursors (a) Ⅰ, (b) Ⅱ and (c) Ⅲ, rolled to 0.126 mm thickness and then heat-treated at 840℃ for 5 h.

fraction of Tl-1223 phase and thus high J_c.

Figs. 3 and 4 show XRD patterns taken in tapes prepared using precursors II and III. The tapes in Figs. 3 and 4 were rolled to 0.216 and 0.126-mm thickness, respectively, and heat-treated at 840℃ for 7 h. Tl-1223 peaks shown in both figures are much less prominent than those in tapes prepared using an unreacted precursor and using an almost same preparation process [20], indicating that volume contents of Tl-1223 phase in both tapes are not large. By the way, the figures show that when the tapes were prepared using same preparation processes, precursor III also resulted in less intense Tl-1212 and $(Sr,Ca)_{14}Cu_{24}O_x$ peaks than did precursor II.

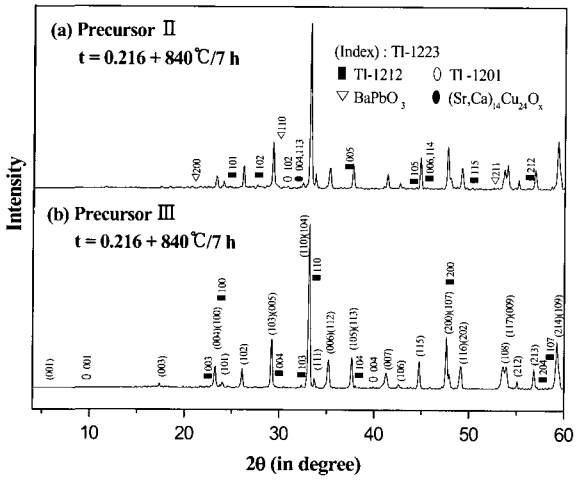


Fig. 3. XRD patterns taken on tapes filled with precursors (a) II and (b) III, rolled to 0.216 mm thickness and then heat-treated at 840℃ for 7 h.

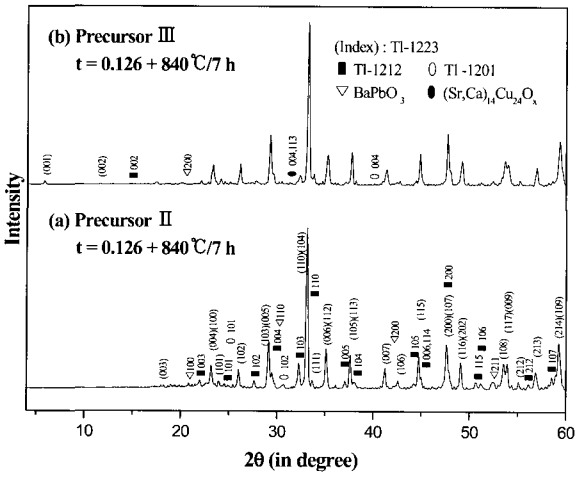


Fig. 4. XRD patterns taken on tapes filled with precursors (a) II and (b) III, rolled to 0.126 mm thickness and then heat-treated at 840℃ for 7 h.

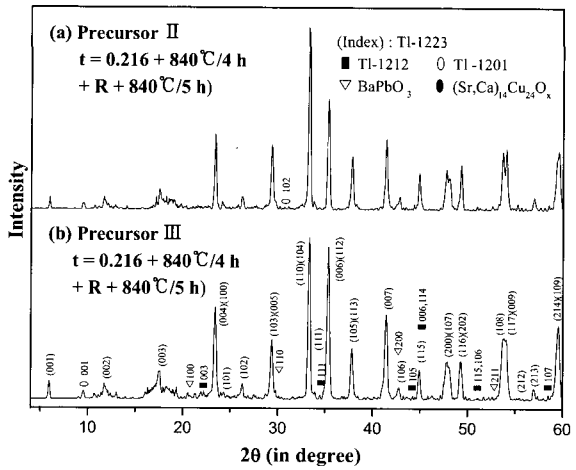


Fig. 5. XRD patterns taken on tapes filled with precursors (a) II and (b) III, rolled to 0.216 mm thickness, heat-treated at 840℃ for 4 h, rolled to 0.115 mm thickness, and then heat-treated for 5 h.

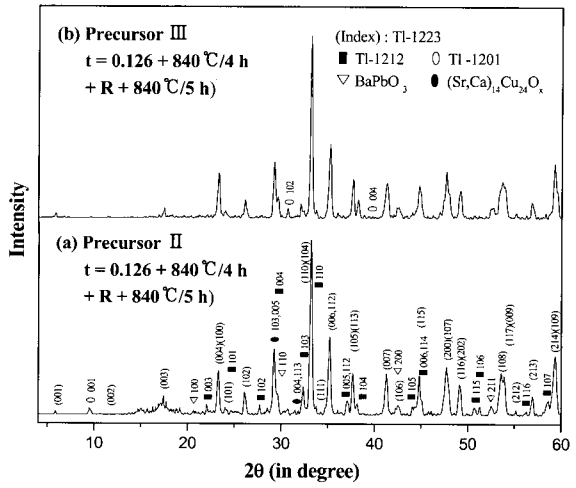


Fig. 6. XRD patterns taken on tapes filled with precursors (a) II and (b) III, rolled to 0.126 mm thickness, heat-treated at 840℃ for 4 h, rolled to 0.105 mm thickness, and then heat-treated for 5 h.

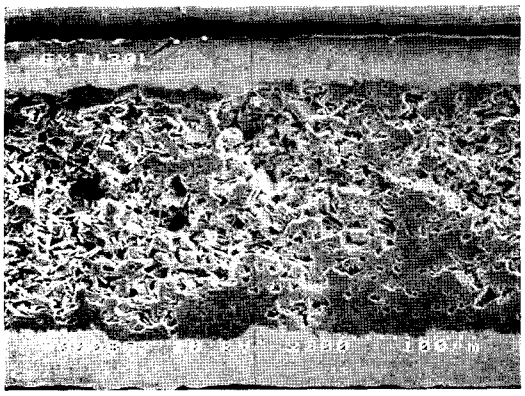
When the tapes were prepared using same precursors but using different degree of mechanical working, more heavily worked tapes contained larger amount of Tl-1212. As J_c appeared higher in more heavily worked tapes, as recognized by comparing Tables 2 and 3, the difference in J_c depending on degree of mechanical working should be attributed not to the difference in Tl-1223 content but to something else, which will be stated later.

Figs. 5 and 6 show XRD patterns taken after final heat-treatment in tapes prepared using precursors II and III and incorporating an intermediate rolling during heat-treatment. The tapes in Fig. 5 were rolled to 0.216-mm thickness, heat-treated at 840℃ for 4 h, rolled to 0.115-mm thickness, and then heat-treated for 5 h. On the other hand, the tapes in Fig. 6 were rolled to 0.126-mm thickness, heat-treated at 840℃ for 4 h, rolled to 0.105-mm thickness, and then heat-treated for 5 h. Note that (00l) peaks of Tl-1223 phase in the figures are much more prominent than those in Figs. 2 to 4. The more prominent (00l) peaks seem to be same ones observed in our previous study [20,21], in which directional-grain-alignment in tapes prepared using an unreacted precursor was much enhanced by incorporating an intermediate rolling during heat-treatment. Therefore, they are believed to be an indication that the intermediate rolling is also highly effective in obtaining directional-grain-alignment and thus high J_c even in the present case of using the reacted precursors. By the way, comparison of Figs. 5 to Fig. 6 reveals that (00l) peak intensities of Tl-1223 phase appeared to be much lower in more heavily worked tapes than in less heavily worked ones. The lower intensities in Fig. 6 indicate that the benefit of intermediate rolling on directional-grain-alignment may be deteriorated when the tapes are heavily worked. In other words, they indicate that there may exist an optimal mechanical working process maximizing the effect of intermediate rolling. Another thing worthwhile to note is that while (00l) peak intensities are higher in Fig. 5(b) than in Fig. 5(a), those in Fig. 6(b) are almost same as in Fig. 6(a). The higher intensities in Fig. 5(b) than in Fig. 5(a) indicate that precursor III results in more enhanced directional-grain-alignment than does precursor II. Thus they imply that there exists an optimal precursor state resulting in a best directional-grain-alignment. In deed, the intensities shown in Fig. 5(b) are a little stronger than those in a tape with J_c of 25,200 A/cm^2 at 77 K and in a self-field prepared using an unreacted precursor in our previous study [20]. However, the almost same intensities in Fig. 6(a) and (b) may indicate that the benefit of using optimum precursor can be diminished or ruled out if the tapes are excessively heavily mechanical-worked

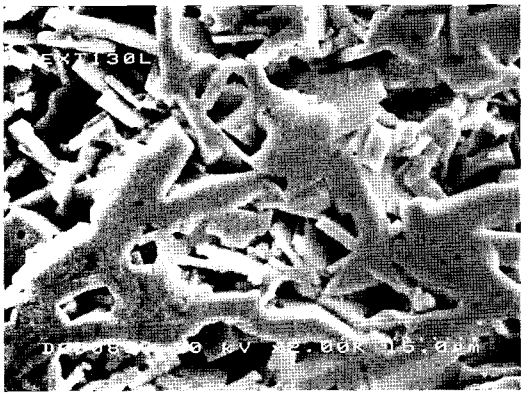
3.4 Scanning electron microscopy

In the present study, the uniformity of interface between Ag sheath and superconducting core, core density, Tl-1223 grain size and the microstructure appeared different, primarily depending on tape thickness, i.e., degree of mechanical working, rather than precursor used, as will be shown later. Only the size of Tl-1223 grains in tapes prepared without incorporating the intermediate rolling appeared to be affected by the precursor used, in addition to tape thickness described previously. The grain size appeared to be larger in precursors I, II and III turn. Figs. 7 and 8 show SEM micrographs taken in tapes with J_c's of 5,600 and 8,010 A/cm^2 at 77 K and in self-fields, which were prepared using precursor III. The tapes in Figs. 7 and 8 were rolled to 0.216 and 0.126-mm thickness, respectively, and heat-treated at 840℃ for 7 h. The figures show a typical interface between Ag sheath and superconducting core, and morphology in tapes prepared without the intermediate rolling. The interfaces are highly non-uniform, compared to those in tapes prepared using an unreacted precursor and using a very similar thermo-mechanical treatment [19,20]. Thus Figs. 7 and 8 indicate that the reacted precursors occur sausages in an earlier stage of mechanical working than the unreacted precursor does. Also the superconducting core is much dense, as recognized by comparing both figures to Fig. 2(a) in ref. [20] and Fig. 3(b) and (c) in ref. [21]. However, Tl-1223 grains in both cases are hardly aligned in preferred orientations.

By the way, comparison of Fig. 7 to Fig. 8 indicates that the interface uniformity and the morphology differed depending on degree of mechanical working prior to heat-treatment. While the less heavily worked tapes revealed relatively uniform interfaces as shown in Fig. 7(a), the more

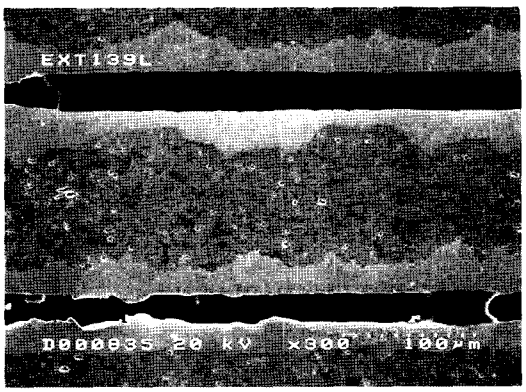


(a)

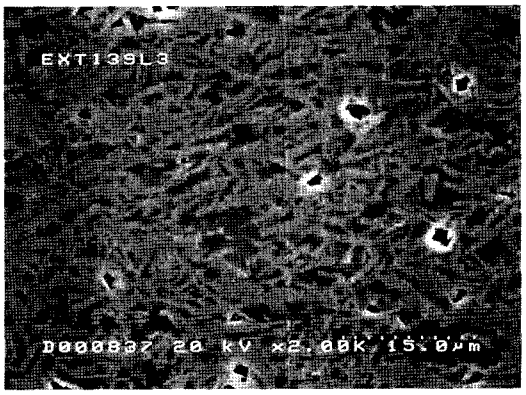


(b)

Fig. 7. SEM micrographs taken in a longitudinal surface of a tape with J_c of 5,600 A/cm^2 at 77 K and in a self field, which was filled with precursor Ⅲ, rolled to 0.216 mm thickness and heat-treated at 840℃for 7 h. (a) Low magnification. (b) High magnification.



(a)



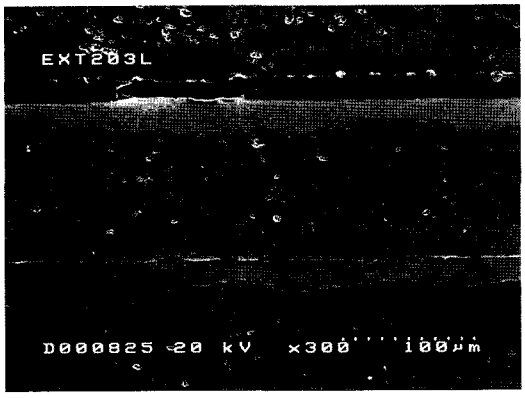
(b)

Fig. 8. SEM micrographs taken in a longitudinal surface of tape with J_c of 8,010 A/cm^2 at 77 K and in a self field, which was filled with precursor Ⅲ, rolled to 0.126 mm thickness and heat-treated at 840℃for 7 h. (a) Low magnification. (b) High magnification.

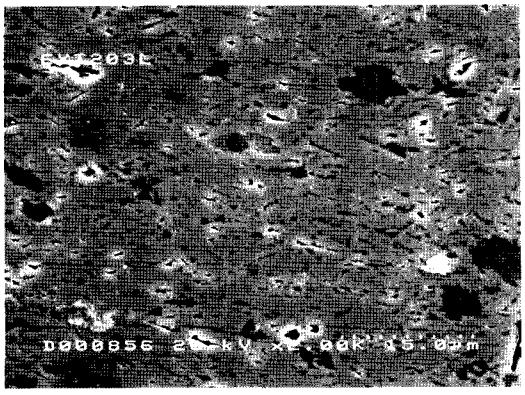
heavily worked tapes did a significantly non-uniform interface shown in Fig. 8(a). The non-uniform interface shown in Fig. 8(a) indicates that significant sausages occurred during rolling from 0.216-mm thickness to 0.126 mm. Also the core density appeared to be higher in the more heavily worked tapes. Thus, higher J_c's in more heavily worked tapes than in less worked ones, which could not be explained in terms of volume content of Tl-1223, are attributed to more excellent grain-connectivity resulting from their higher core density. Another feature to be noted by comparing Fig. 7 to Fig. 8 is that the size of Tl-1223 grain appeared to be quite different depending on degree of mechanical working While the grain size in Fig. 7(b) are estimated to 10~12 μm, that in Fig. 8(b) are 6~7 μm. In addition to stronger Tl-1212 peaks in Fig. 4(b) than in Fig. 3(b), the smaller grain size in Fig. 8(b) than in Fig. 7(b) may imply that the growth of Tl-1223 grains in tapes heavily worked is retarded. However, no noticeable difference in directional grain-alignment between both tapes was observed. Both tapes reveal poor directional-grain-alignment, as shown in Fig. 7(b) and Fig. 8(b).

Figs. 9 and 10 show SEM micrographs taken in tapes with J_c's of 21,450 and 8,090 A/cm^2,

respectively, at 77 K and in self fields, which were prepared using precursor Ⅲ. The tape in Fig. 9 was rolled to 0.216-mm thickness, heat-treated at 840℃ for 4 h, rolled to 0.115-mm thickness, and then heat-treated for 5 h. On the other hand, the tape in Fig. 10 was rolled to 0.126-mm thickness, heat -treated at 840℃ for 4 h, rolled to 0.115-mm thickness, and then heat- treated for 5 h. The figures show typical interfaces and the morphology in tapes prepared by using reacted precursors and incorporating an intermediate rolling during heat -treatment. The interfaces are highly non-uniform, compared to those in tapes prepared using an unreacted precursor and using a very similar thermo -mechanical treatment [19,20]. In both figures, however, the superconducting cores are highly dense. They are much denser than that in the tape with J_c of 25,200 A/cm^2 at 77 K and in a self-field prepared using an unreacted precursor in our previous study [20, 21], so that Tl-1223 grains seem to be connected more tightly. Also the density of impurities seems to be lower.

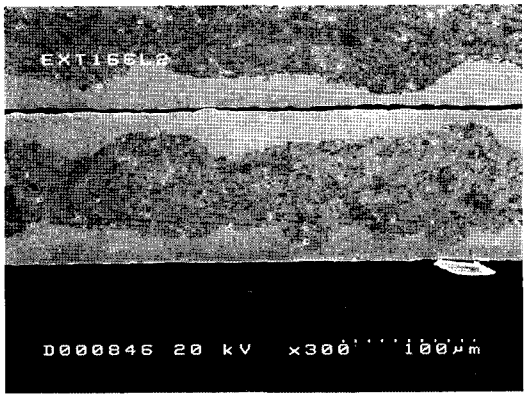


(a)

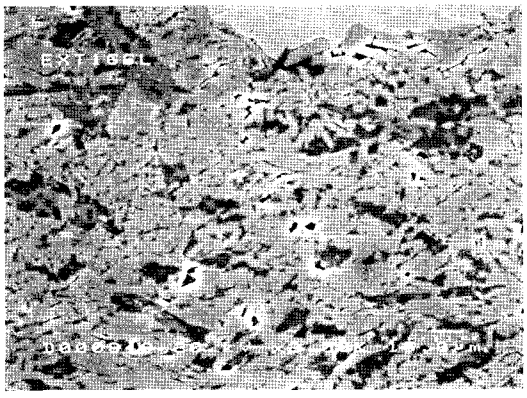


(b)

Fig. 9. SEM micrographs taken in a longitudinal surface of a tape with J_c of 21,450 A/cm^2 at 77 K and in a self field, which was filled with precursor Ⅲ, rolled to 0.216 mm thickness, heat-treated at 840℃ for 4 h, roll to 0.115 mm thickness and then heat-treated for 5 h. (a) Low magnification. (b) High magnification.



(a)



(b)

Fig. 10. SEM micrographs taken in a longitudinal surface of tape with J_c of 8,090 A/cm^2 at 77 K and in a self field, which was filled with precursor Ⅲ, rolled to 0.126 mm thickness, heat-treated at 840℃ for 4 h, roll to 0.105 mm thickness and then heat-treated for 5 h. (a) Low magnification. (b) High magnification.

By the way, comparison of Fig. 9 to Fig. 10 reveals that the uniformity of the interface between Ag and superconducting core and directional-grain-alignment appeared to be quite different depending on degree of mechanical working applied during the tape preparation. The less heavily worked tapes showed relatively more uniform interfaces as shown in Fig. 9(a) and a more textured microstructure as shown in Fig. 9(b). The texture shown in Fig. 9(b) is more excellent than that in the tape with J_c of 25,200 A/cm^2 at 77 K and in a self-field prepared using an unreacted precursor in our previous study [20, 21]. The excellent texture is in a good agreement with very prominent (00l) peaks of Tl-1223 shown in Fig. 5(b). On the other hand, the more heavily worked tapes showed highly non-uniform interfaces as shown in Fig. 10(a), and relatively poor directional-grain-alignment as shown in Fig. 10(b). Highly non-uniform interface shown in Fig. 10(a) indicates that the sausages shown in Fig. 8(a) were aggravated during intermediate rolling. It is believed that the aggravated sausages significantly caused Tl-1223 grains to be misarranged out of tape-length direction, especially in regions near the interface. Such a misalignment is likely to be responsible for the reduced intensities of (00l) peaks of Tl-1223 shown in Fig. 4.

3.5 Magnetic field dependence of transport J_c

Fig. 11 shows the dependence of I_c at 77 K on magnetic field measured in tapes with J_c's of 18,670 (tape A) and 21,450 A/cm^2 (tape B) at 77K and in self-fields. Tape A was filled with precursor Ⅱ, rolled to 0.216-mm thickness, heat-treated at 840℃ for 3 h, rolled to 0.115-mm thickness, and then heat-treated for 5 h. Tape B was filled with precursor Ⅲ, rolled to 0.216 mm thickness, heat-treated at 840℃ for 4 h, rolled to 0.115 mm thickness, and then heat-treated for 5 h. The figure shows that there exist significant weak-links in both tapes. I_c's of tapes A and B begin to saturate to 4.2 and 3.3%, respectively, of $I_c(0)$ near 3,000 Oe. The values of $I_c/I_c(0)$ at the saturation field in both tapes is higher than 2% in tape with J_c of 25,200 A/cm^2 at 77 K and in a self-field prepared using an unreacted precursor [20,21]. The higher values may indicate that Tl-1223 grains in the present tapes are more tightly connected due to enhanced core density as shown in Fig. 9(b), and thus a relatively larger portion of inter-granular contacts survives under high fields.

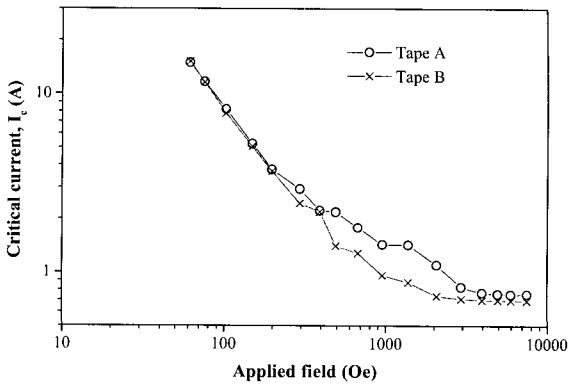
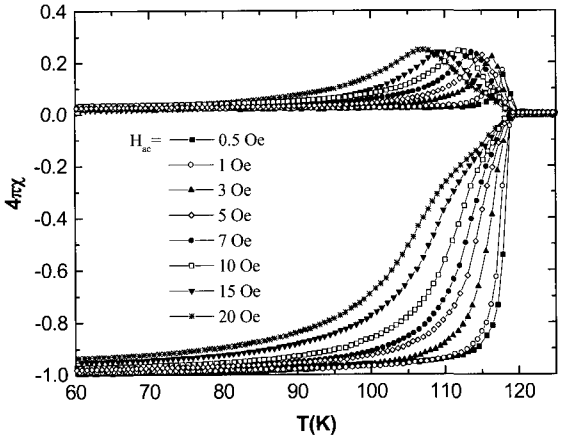


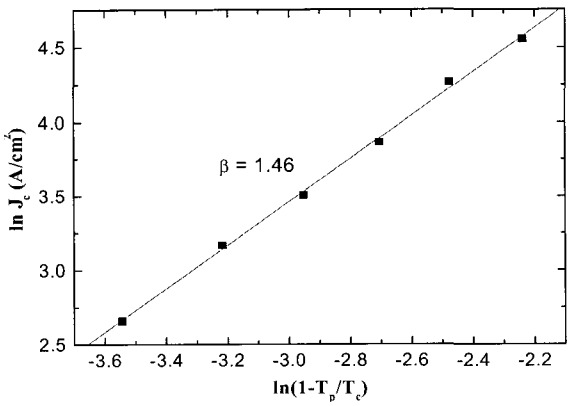
Fig. 11. The dependence of J_c at 77 K on magnetic field measured in tapes with J_c's of 18,670 (tape A) and 21,450 A/cm^2 (tape B) at 77K and in self-fields. Tape A was filled with precursor Ⅱ, rolled to 0.216 mm thickness, heat-treated at 840℃ for 3 h, rolled to 0.115 mm thickness, and then heat-treated for 5 h. Tape B was filled with precursor Ⅲ, rolled to 0.216 mm thickness, heat-treated at 840℃ for 4 h, rolled to 0.115 mm thickness, and then heat-treated for 5 h.

3.6 Inter-granular J_c and junctional characteristic

Fig. 12(a) shows the temperature dependence of ac susceptibilities measured at selected fields in a tape with J_c of 21,450 A/cm^2, which was filled with precursor Ⅲ, rolled to 0.126 mm thickness, heat-treated at 840℃ for 4 h, rolled to 0.115 mm thickness, and then heat-treated for 5 h. Fig. 12(b) shows the $(1-T_p/T_c)$ dependence of J_c calculated by applying the temperatures, T_p, at which maximum ac loss appears at the applied ac field in Fig.12(a), to the critical state formula $J_c \cong H_m/a$ in the framework of 'finite temperature critical state model' for granular superconductors [24-26], where T_c is the critical transition temperature, which is estimated to 119 K, H_m magnitude of the applied field and a the specimen dimension. From Fig. 12(b), the β value in $J_c(T) \propto (1-T/T_c)^{\beta}$ [27,28], which indicates the junctional characteristic of inter-granular contacts, is estimated to 1.46. The β value indicates that the inter-granular contacts in the present tapes are a mixed type of SIS and SNS junctions. The β value in the present study



(a)



(b)

Fig. 12. (a) Temperature dependence of ac susceptibilities measured at selected fields in a tape with J_c of 21,450 A/cm^2, which was filled with precursor III, rolled to 0.126 mm thickness, heat-treated at 840℃ for 4 h, rolled to 0.115 mm thickness, and then heat-treated for 5 h. (b) $(1-T_p/T_c)$ dependence of J_c calculated by applying Fig. 14(a) to the critical state formula $J_c \cong H_m/a$, where T_p is the temperature at which maximum ac loss appears in a given applied field, H_m magnitude of the applied field and a the specimen dimension.

is higher than that in the tape with J_c of 25,200 A/cm^2 prepared using unreacted precursor in our previous study [20,21]. It indicates that the inter-granular junctional characteristic was shifted to more SNS type as a result of the increase in core density by using reacted precursors. The higher β may suggest that the inter-granular coupling among Tl-1223 grains becomes stronger by using reacted precursors.

IV. Discussion

In the present study, much dense and highly textured Tl-1223/Ag tapes were prepared by using reacted precursors, compared to those prepared using an unreacted precursor [20,21]. The details of experimental findings resulting from using the reacted precursors are summarized as follows:

Firstly, when the tapes were prepared without incorporating the intermediate rolling, the reacted precursors resulted in relatively much low Tl-1223 content and J_c's, highly non-uniform interface, but much dense tape cores. No trace for directional grain-alignment was observed. Secondly, when the tapes were prepared by incorporating the intermediate rolling during heat-treatment, the reacted precursors resulted in a little more intense (00l) peaks, highly non-uniform interface, much dense core and highly textured microstructure, but they did relatively low J_c's. As results of enhanced densification and grain texturing, the fraction of strong-links in the tapes was doubled and thus the field dependence of their J_c became weaker. Also the junctional characteristic of inter-granular contacts among neighboring Tl-1223 grains was shifted to more SNS one.

Then, questions on why and how the reacted precursors give rise to such results arise. The possible conjectures are as follows:

Much dense cores in the present study can be considered to originate from high physical densities of the constituent particles of the reacted precursors, the presence of Tl-1212 and Tl-1223 platelets in the reacted precursor, and the suppressed volume expansion due to reduced evaporation of volatile elements from the reacted precursors, as follows: As the physical densities of the constituent particles of the reacted precursors are believed relatively high, they are likely to result in relatively high core density after mechanical working, provided the compaction density of the core filled with the reacted precursors is comparable to that filled with unreacted one. By the way, Tl-1212 and Tl-1223 platelets contained in the reacted precursors are likely to be directionally

aligned in a certain extent during mechanical working, and decrease the porosity, resulting in a relatively high compaction density. Accordingly, the core density after mechanical working is expected to be high. Furthermore, as the volatile elements in the reacted precursors are present as constituent elements of compounds, their vapor pressures during heat-treatment are expected to be very low. The much low vapor pressure makes the swelling of tape core during heat-treatment negligible. Therefore, the resultant core density would be very high compared to that in the case of using unreacted precursor. However, little directional-grain-alignment in Fig. 7 and 8 indicates that the contribution of pre-alignment of Tl-1212 and Tl-1223 platelets to the dense tape core is not so great.

The highly non-uniform interface is thought to originate from high mechanical strength of constituent particles of the reacted precursors. The mechanical working is a process of compaction of constituent particles in the precursor, which occurs by powder flow in the initial stage and then by fracture and fragmentation of constituent particles followed by rearrangement of fractured particles and fragment. Even though the mechanism for the sausage formation is not elucidated yet, the sausages are believed to form by discrete displacement of the particles developed by the difference in mechanical strength between Ag and oxide particles when compaction occurs by fracture and fragmentation followed by rearrangement. By the way, as the reacted precursors contain particles of reaction products, their densities and thus their mechanical strength are likely to be higher than those of unreacted precursor. So the fracture and the fragmentation of particles in the reacted precursor require higher stresses than do those in unreacted one. The high stresses are apt to result in highly discrete displacement of the particles and thus to form sausages. Furthermore, the high compaction density mentioned above is believed to facilitate the sausage formation in an early stage of mechanical working.

The highly textured microstructure is thought to result from high densities of the reacted precursors, and the presence of Tl-1212 and Tl-1223 platelets and fine dispersion of Tl-1212 and Tl-1223 platelets and secondary phases in the reacted precursors. As the reacted precursors contain finely dispersed Tl-1212 and Tl-1223 platelets and secondary phases, the Tl-1223 platelets are likely to be directionally and uniformly grown during the first heat-treatment, compared to the case of using unreacted precursor. Also it is likely that the secondary phases with relatively small sizes finely dispersed after the first heat-treatment. Also high densities of the reacted precursors resulted in much dense cores, as mentioned in a previous paragraph. Then inter -mediate rolling and the second heat-treatment are likely to result in better directional alignment of Tl-1223 grains, due to much low density of pores and secondary phases with reduced sizes, which are known to hinder directional-grain-alignment in local regions.

As results of the much enhanced core density mentioned above, inter-granular contacts in the tape appeared to be shifted to a more metallic type. Furthermore, the fraction of the strong-links increased by twice. These experimental observations suggest that the inter-granular junctional characteristics depend not on superconducting material but on the core density.

Despite of highly dense morphology and textured microstructure, by the way, relatively low J_c's in the present study were obtained, compared to those in tapes prepared using unreacted precursor. They are attributed to low content of Tl-1223 resulting from the deficiency of Tl, Pb and Bi element in the reacted precursors. However, a J_c as high as 21,450 A/cm^2 could be obtained by using precursor Ⅲ, in which the molar ratios of Tl, Pb and Bi appeared to be relatively nearer to the stoichiometric ratio of Tl-1223 than in precursors Ⅰ and Ⅱ, suggesting that tapes with much higher J_c's may be prepared provided the stoichiometric ratio of the constituent elements in the precursors are properly controlled.

By the way, these results are considerably contrary to those of Selvamanickam et al. [11]. The totally different results are believed to originate from the difference in phase contents between the reacted precursors. During final heat-treatment, the precursors in the present study could supply sufficient liquid phases necessary to heal out cracks generated during intermediate rolling [29], whereas their precursors could not. Note that there exist no noticeable cracks in Figs. 7 to 10. The detailed preparation history of the reacted precursors in their

paper is not known. However, supply of liquid phases by using not a sintering process but partial melting for final heat-treatment indicates that their precursors might be heat-treated for a relatively long time so that little ingredients necessary for formation of liquid phases during final heat-treatment were left. On the other hand, as the precursors used in the present study were heat-treated only for a short time of 20 min, they might have sufficient ingredients. Therefore, the improved morphology including enhanced grain-connectivity is attributed to sufficient crack heal-out, in addition to the reduced core density.

In conclusion, the present study reveals that the grain-connectivity can be much improved by using the reacted precursors, provided that the phase content of the reacted precursor and the detailed preparation process are properly controlled.

V. Conclusion

Three kinds of precursors were prepared by heat-treating a mixture of Sr-Ba-Ca-Cu-O, Tl_2O_3, PbO and Bi_2O_3 powders at 805 (precursor Ⅰ), 840 (precursor Ⅱ) and 905℃(tape Ⅲ), respectively, for 20 min and then grinding finely. The effects of the reacted precursors on phase evolution, microstructure, J_c and junctional characteristic of the inter-granular contacts were investigated in Ag-sheathed Tl-1223 tapes filled with three kinds of precursors and heat-treated with an intermediate rolling, and compared to those in the tape prepared using an unreacted precursor. As a result, it was found that Tl-1223 phase content, grain size and J_c in the tapes primarily depended on tape thickness, namely degree of mechanical working prior to heat-treatment, and were high in precursors Ⅰ, Ⅱ and Ⅲ turn. Also the growth of Tl-1223 was retarded when the tapes were excessively worked prior to heat-treatment. Compared to tapes prepared using an unreacted precursor, more excellent texture was obtained in tapes prepared using precursors Ⅱ and Ⅲ. It was attributed to reduced pore and impurity densities resulting from using the reacted precursors. Also characteristic of inter-granular contacts and fraction of strong-links were improved. They are attributed to enhanced grain-connectivity resulting from their highly dense morphology. The β=1.46 value in $J_c(T) \propto (1-T/T_c)^{\beta}$ estimated from ac susceptibilities indicated that the inter-granular contacts are composed of a mixed type of SIS and SNS junctions. A relatively low J_c of 21,450 A/cm^2 at 77 K and in a self field, compared to that in the tape prepared using an unreacted precursor, was obtained in a tape prepared using precursor Ⅲ, due to relatively thick thickness of the tape. However, the highly textured and dense microstructure obtained in the present study suggests that Tl-1223 tapes with much higher J_c may be prepared by using the reacted precursors, provided that a proper thermo-mechanical process is used.

Acknowledgments

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