Controlling the secondary phase of BSCCO 2223 tapes by thermal slide heat treatment(TSHT)

Sung-Chang Park*, Jai-Moo Yoo*, Jae-Woong Ko*, Young-Kuk Kim* and Cheol-Jin Kim**

* Materials Technology Dept., Korea Institute of Machinery & Materials
** Dept. of Ceramic engineering, Gyeongsang National University

amadeous@orgio.net

Abstract– The phase transformation, variation of secondary phase, and critical current density (J_c) for $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ (2223) tapes have been studied through the thermal slide heat treatment (TSHT) process. This process consists of a multiple variations of oxygen partial pressures and temperatures at the initial heat treatment. During the initial heat treatment, some secondary phases such as $(Ca,Sr)_2CuO_3$ (2/1 AEC), $(Ca,Sr)_{14}Cu_{24}O_{41}$ (14/24 AEC), and $(Bi,Pb)_2Sr_2CuO_y$ (2201, amorphous phase) form in Bi-2223 tapes, especially at the 2223 grain boundaries. These secondary phases are detrimental to the phase transformation and final properties. In order to control the secondary phase in Bi-2223 tapes the amount and size of secondary phases among the TSHT process were observed. The results indicate that the amount and particle size of AEC particles were smaller when the TSHT process was used than when the normal process at the initial heat treatment was used, which results in the improved J_c properties after the final process.

1. INTRODUCTION

The formation of the 2223 phase is considered to proceed by reactions between $Bi_2Sr_2Ca_1Cu_2O_y$, alkaline earth cuprate(AEC), and liquid phase[1]. Many works on the influence of secondary phases, phase assemblage, carbon content, lead variations, and particle size distributions of BSCCO tapes have been studied [2]-[4]. One of the most important current limiting factors, is the presence of secondary phases in the tapes after heat treatment, such as $(Ca,Sr)_2CuO_3$ (2/1 AEC), $(Ca,Sr)_{14}Cu_{24}O_{41}$ (14/24 AEC), and $(Bi,Pb)_2Sr_2CuO_y$ (2201, amorphous phase).

It was difficult to remove these phases from the BSCCO 2223 matrix during the normal heat treatment. These secondary phases degrade the critical current density. In order to control the amount and size of AEC particles, thermal slide heat treatment (TSHT) was applied during the initial heat treatment under the varying atmosphere. Also, the effect of the secondary phases on the transport properties was investigated.

2. EXPEPIMENTAL

The precursor powders have nominal cation ratio of

Bi:Pb:Sr:Ca:Cu=1.8:0.3:2.0:2.2:3 which consist of BSCCO-2212 as the major phase. These precursor powders were made into 61 filament Bi-2223/Ag tapes using the standard PIT method with repeated drawing and rolling steps.

The wire was drawn into 1.5mm and cold rolled into a tape with thickness of $250\,\mu m$ and 4 mm width. Thereafter, tape samples(~ 4 cm in length) were annealed at 843 ℃ under various atmosphere. All samples were heat treated in various atmosphere using two thermal cycles with TSHT process at the initial heating cycle as described schematically in Fig. 1.
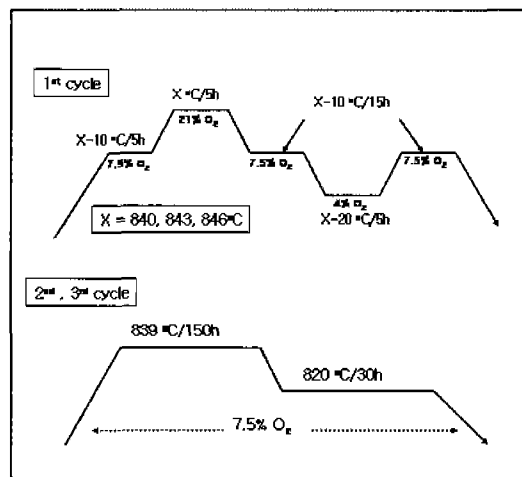

Fig. 1. Schematic illustration of the experimental procedure of the heat treatment

After the final heat treatment, the critical current I_c was measured at 77K in self field by standard four-point method with criterion of 1 $\mu V\ cm^{-1}$.

Microstructural and compositional analysis was performed on the longitudinal cross sections of samples using XRD, SEM, and EDS. The particle size and area fraction of AEC phases were quantified in the SEM secondary micrographs using an image processing program IMAGE-PRO. The relative error of the area fraction measurement was ±3%.

The percentage of Bi-2223 phase in the phase mixture, $X_{Bi-2223}$, was defined by (1), where $I_{Bi-2223}$ and $I_{Bi-2212}$ are integrated intensities of X-ray diffraction $(00\underline{10})$ peak of Bi-2223 phase and (008) peak of Bi-2212 phase, respectively[5].

$$X_{Bi-2223} = (I_{Bi-2223}) / (0.88 I_{Bi-2212} + I_{Bi-2223}) \qquad (1)$$

3. RESULTS AND DISCUSSIONS

Table I. gives critical current density by a temperature variation and holding time. The secondary phases could be identified in the XRD spectrum.

TABLE I
J_c PROPERTIES AFTER FINAL HEAT TREATMENT.

Temp.	Sintering time	Critical current density (J_c)	measurity condition
840℃	50h	9,280 A/cm²	77K, 0T
	200h	20,690 A/cm²	
	300h	21,300 A/cm²	
843℃	50h	12,425 A/cm²	77K, 0T
	200h	28,170 A/cm²	
	300h	27,200 A/cm²	
846℃	50h	7,840 A/cm²	77K, 0T
	200h	19,320 A/cm²	
	300h	18,500 A/cm²	

After heat treatment, there were 2201, Ca_2PbO_4, $(Ca,Sr)_{14}Cu_{24}O_z$ (14:24), $(Ca,Sr)_2CuO_3$ (2:1) and CuO in the tape. The area fractions of these phases are shown as a function of sintering time(h) in Fig. 2. After the initial heat treatment, more 2:1 AEC particles exist than 14:24 AEC. These 2:1 AEC particles react with liquid phase (2201 phase) at the second heat treatment, and then 2223 phase is formed. At the TSHT process[6], we chose processing atmospheres of 7.5% O_2 (because it ensures the best conversion rates to BSCCO 2223), 21% O_2 (because 2:1 AEC and CuO tend to decompose at high oxygen partial pressure and temperature), and 4% O_2 (because 14:24 AEC was found to be unstable at low oxygen partial pressure and temperature).
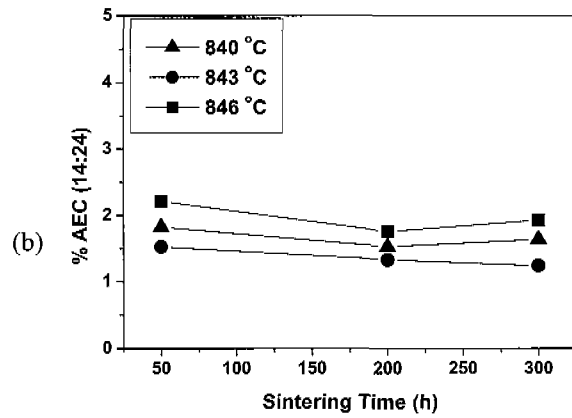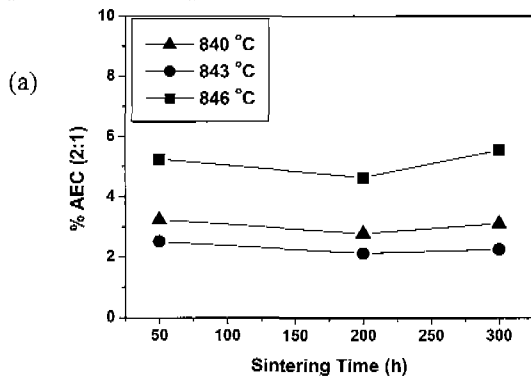

(a)

Fig. 2. (a) The area fractions of 2:1 AEC particles, and (b) the area fractions of 14:24 AEC particles after heat treatment.

As can be seen in Fig. 3(a), ~94% BSCCO-2223 phase formed after the second heat treatment. J_c values start to drop after the third heat treatment in all the tapes. The highest J_c value, 28,170 A/cm² (77 K and 0 T), was achieved in the sample heat treated at 843 ℃ for 200h with one intermediate rolling during the second heat treatment (Fig. 3(b)).
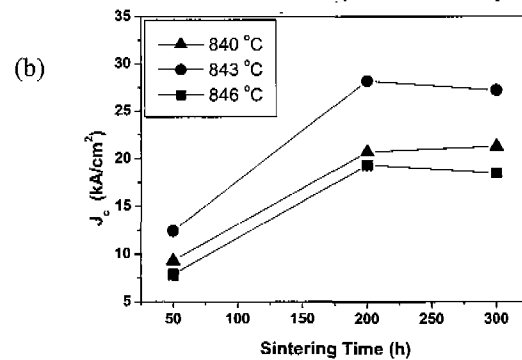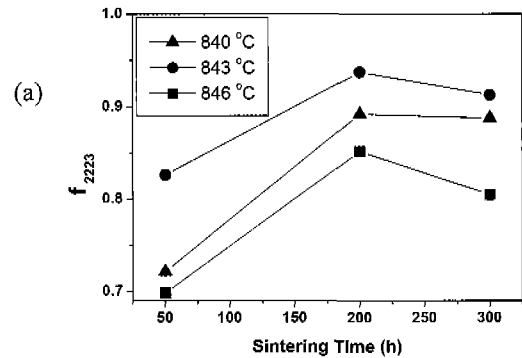

(a)

(b)

Fig. 3. (a) The area fractions of 2223 phase, and (b) J_c at 77K, zero applied field as a function of sintering time

In table II. the area fraction of the various secondary phases at different heat treatment stage are presented, which were determined using XRD, EDS, and image analysis software(IMAGE PRO™). Usually, at the initial heat treatment AEC particle sizes become large (2:1AEC; 2-5μm, 14:24AEC; 5-10μm). Whereas, TSHT processes with proper condition resulted in smaller particles sizes (2:1AEC; <2μm, 14:24AEC; <5μm).

TABLE II
THE AREA FRACTION OF THE SECONDARY PHASES (843 $\degree$C TSHT PROCESS)

	1st H.T.	2nd H.T.	3rd H.T.
2:1 AEC	2.512	2.125	2.258
14:24 AEC	1.525	1.328	1.236
Ca$_2$PbO$_4$	0.187	0.077	0.183
2201	0.126	0.08	0.112
3221	0.865	0.213	1.705
Total %	5.215	3.823	5.494

Fig. 4(a) shows the area fraction of the secondary phases after final heat treatment. The SEM micrographs from polished and etched longitudinal cross-section of final tapes are illustrated in Fig. 4(b) ~ 4(d).
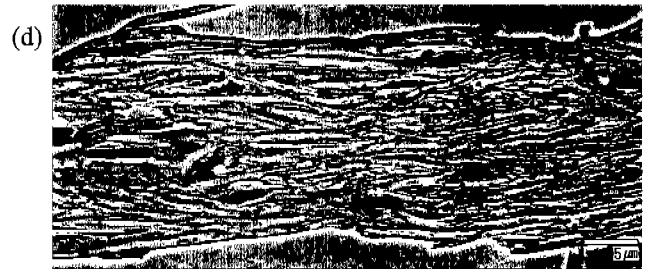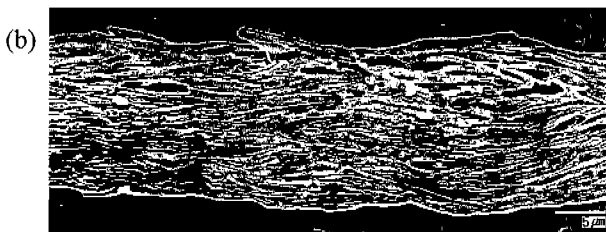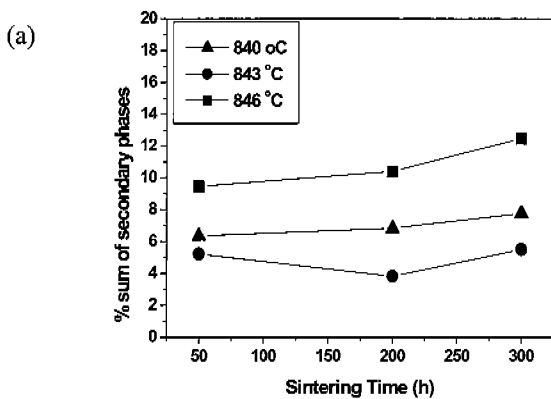
(a)

(b)

(c)

(d)

Fig. 4. (a) The area fractions of total secondary phases, SEM micrographs from polished and etched longitudinal cross-section of fully processed samples (TSHT processes) (b) 840 $\degree$C, (c) 843 $\degree$C, and (d) 846 $\degree$C.

It can be seen that Fig. 4(c) shows the improved grain size, grain alignment of 2223 phase(shape of needle like), and better core density compared with Fig. 4(b) and 4(d). The tape in Fig. 4(d) contains liquid phase (2201 phase) and misoriented grains together with large amount of AEC phase. Also, Pb-rich secondary phase (3221 phase, Bi$_{0.5}$Pb$_3$Sr$_2$Ca$_2$CuO$_x$) appeared in the tape.

4. CONCLUSION

In this study, the area fraction and the size of AEC particles during the heat treatment, microstructure and transport properties of BSCCO-2223/Ag tapes have been studied. Microstructural characterization with SEM and XRD gave evidence that controlling the secondary non-SC phases, such as (Ca,Sr)$_2$CuO$_3$ (2/1 AEC), (Ca,Sr)$_{14}$Cu$_{24}$O$_{41}$ (14/24 AEC), and (Bi,Pb)$_2$Sr$_2$CuO$_y$ (2201, amorphous phase) are important for 2223 formation. After initial heat treatment with TSHT method, secondary phase decreased and 2223 volume fraction increased. The best aligned BSCCO 2223 grains were formed after the second heat treatement at 843 $\degree$C TSHT condition and 200hrs holding time. This process resulted in the value of J$_c$ as high as 28,170 A/cm^2 with a small AEC phases.

REFERENCES

[1] J. A. Parrell, Y. Feng, "Controlled decomposition and reformation of the 2223 phase in Ag-clad (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ tapes and its influence on the microstructure and critical current density." Journal of materials Research. Vol. 11, No. 3. March 1996.

[2] T. Haugan, "Partial-Melt Growth of Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$/Ag Superconducting Tapes," PhD Dissertation, State Univ. of New York at Buffalo, UMI Dissertation Services, Ann Arbor MI, USA, 1995.

[3]   Lujn Wu, Yimei Zhu, M. Suenaga, "Crystallographic analysis of the
       intermediate phases observed during the conversion of $(Bi,Pb)_2Sr_2$
       $CaCu_2O_{8-\delta}$ to $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ in composite tapes," Physica
       C 305 167-178, 1998.

[4]   Lujn Wu, Yimei Zhu, M. Suenaga, "Crystallographic analysis of the
       intermediate phases observed during the conversion of $(Bi,Pb)_2Sr_2$
       $CaCu_2O_{8+\delta}$ to $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ in composite tapes," Physica
       C 305 167-178, 1998.

[5]   S. Li, Q. Y. Hu, H. K. Liu, S. X. Dou and W. Gao, "The grain
       alignment of Bi2223, Bi2212 and Bi2223+Bi2212 phases in
       mechanical deformation and annealing processes" Physica C 279,
       265-276, 1997.

[6]   R. M. Baurceanu, V. A. Maroni, N. N. Merchant, A. K. Fischer, M. J.
       McNallan and R. D. Parrella, "Time evolution of phase composition
       and microstructure in the Ag/Bi-2223 composite superconductor
       heat-treated at specific pO_2/temperature set points" , Supercond. Sci.
       Technol. 15. 1160-1166. 2002.