Journal of the Korea Institute of Applied Superconductivity and Cryogenics
Vol.5, No.1, (2003), pp. 31~34

Effect of pre-annealing conditions on critical current density of Bi-2223 tapes

Dong-Woo Ha, Joo-Saeng Yang, Hong-Soo Ha, Sang-Soo Oh, Dong-Hoon Lee, Sun-Yuk Hwang, Jung-Gyu Choi and Young-Kil Kwon

Applied Superconductivity Group, Korea Electrotechnology Research Institute

dwha@keri.re.kr

Abstract-- **Bi-2223 superconducting wires with 55 filaments were fabricated by stacking, drawing process with different heat-treatment histories. Two kinds of powders were prepared. One was pre-annealed at 760 - 820 ℃ and low oxygen partial pressure, and the other was only calcined state. Before rolling process, round wires were pre-annealed at 760 - 820 ℃ and in a low oxygen partial pressure. We confirmed that pre-annealing step was to transform Bi-2212 orthorhombic structure from Bi-2212 tetragonal structure and to reduce the formation of second phases at superconducting wire. However Bi-2223 phases were formed at higher pre-annealing temperature. Bi-2223 conductor was needed frequently annealing at low temperature because pre-annealing at precursor powder brought about decrease in workability. We could achieve highest Je of 6500 A/cm^2 at the tape using Bi-2212 orthorhombic phase by introduced slightly overheating at the 1st sintering process.**

1. INTRODUCTION

Many of research efforts have been focused on the improvement of critical current density Jc of silver-sheathed Bi-2223 tapes for practical applications of this material. Large and well c-axis oriented grains, better grain connectivity, higher formation of Bi-2223 phase together with minimized secondary phase in final reacted tapes were considered to be beneficial to carry large transport currents [1,2]. Bi-2223 phase is formed by the solid-state reaction with Bi-2212, Ca_2PbO_4, CuO, and $(Sr,Ca)_{14}Cu_{24}O_x$ phases during heat treatment. However, it is difficult to form Bi-2223 completely through this reaction because the rate of Bi-2223 formation is low and temperature range to produce Bi-2223 phase is narrow. Besides, a lot of voids and impurity phases (2201, 2212, 3221, $(Sr,Ca)_{14}Cu_{24}Ox$, Ca_2PbO_4, Ca_2CuO_3, CuO) are remained after this reaction[3,4]. If the formation of impurity phases can be decreased, critical current density will be increased. it was reported that critical current density could be improved through the transformation of Bi-2212 phase of precursor powder to orthorhombic structure from tetragonal structure before rolling process [5].

In this study, the transformation of Bi-2212 phase was investigated, which was transformed to orthorhombic from tetragonal through pre-annealing during powder packing and drawing process. The relationship between hardness of Bi-2212 orthorhombic phase and workability of Bi-2223/Ag tape was investigated. Microstructure and critical current density of pre-annealed Bi-2223 superconducting tapes were also investigated.

2. EXPERIMENTAL

Precursor powders with nominal composition of $Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{2.0}Cu_{3.0}O_x$ were put into pure silver (Ag) tube and drawn to hexagonal mono filamentary state. Using these mono core composites, 55 filaments Bi-2223/Ag tapes were fabricate by the well-established powder-in-tube method. Round wires of intermediate state of drawing process were pre-annealed specially from 760 ℃ to 820 ℃ for 2 h at low oxygen partial pressure in order to form orthorhombic Bi-2212 structure from tetragonal Bi-2212 structure. Round wires were rolled with various reduction ratio to investigate workability. The short pieces of tapes cut from the as-rolled long tapes were sintered at 830 ℃ and 8% oxygen in argon. The critical current was measured at 77 K and 0 T by the standard four-probe method with a criterion of 1V/cm. X-ray diffraction (XRD) measurements were performed on longitudinally peeled samples. The cross sections of reacted tapes were observed using an optical microscope and a scanning electron microscope (SEM). The hardnesses of cross sections of round wires were measured during working process.

3. RESULT AND DISCUSSION

The pre-annealing was performed at 760 ℃ and 0.1% oxygen in nitrogen for 2 hours with 2 different conditions to investigate transformation of Bi-2212 phase. One is Bi-2212 precursor powder state before powder packing, and other is round wire state before rolling.

Fig.1 plots the XRD patterns of pre-annealed precursor powder (PA) and original precursor powder (PN). It is clear that the peaks of Ca_2PbO_4 phase (2θ =17.7°,CP) are decreased and the peak split phenomenon is created at the peak of 33° (2θ). These results show Bi-2212 phase of precursor powder is transformed to orthorhombic structure from tetragonal structure after pre-annealing.

There are some differences between XRD patterns of precursor powder and those of round wire state. Fig.2 plots

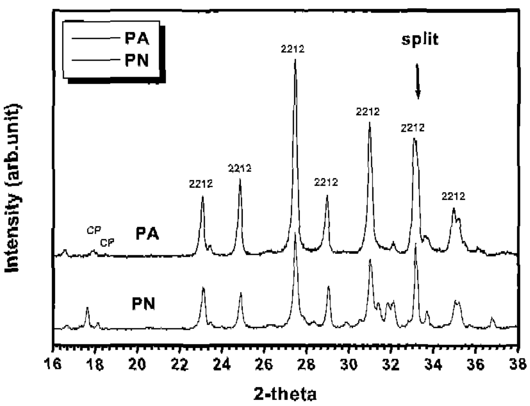


Fig. 1. XRD patterns of pre-annealed precursor powder (PA) and original precursor powder (PN).

the XRD patterns of pre-annealed round wire and not annealed round wire, which are prior to rolling. The peak shapes of round wire are broader than those of precursor powder. The decrease of Ca_2PbO_4 peak intensity after pre-annealing was similar to the result of Fig. 1. The peaks at 2θ values of 23°, 29°and 35° are relatively higher than other peaks, which are related to Bi-2212 orthorhombic structure. So, It was confirmed that Bi-2212 phase was transformed to orthorhombic structure from tetragonal structure not only precursor powder state but also round wire state.

Fig.3 plots the XRD patterns of round wires pre-annealed at various temperatures - 760, 790 and 820 ℃, which are prior to rolling. Bi-2223 peaks are observed for the specimens pre-annealed over than 790℃. Therefore, pre-annealing at higher temperature was found to promote the formation of Bi-2223 phase besides transformation to Bi-2212 orthorhombic structure.

The hardness of the wire that used pre-annealed precursor powder was investigated to know the relationship between Bi-2212 orthorhombic structure and. workability during drawing process. The Vicker's hardness values

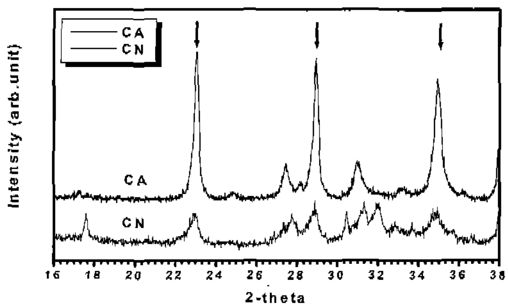


Fig. 2. XRD patterns of pre-annealed round wire (CA) and not annealed ound wire (CN), which are prior to rolling.

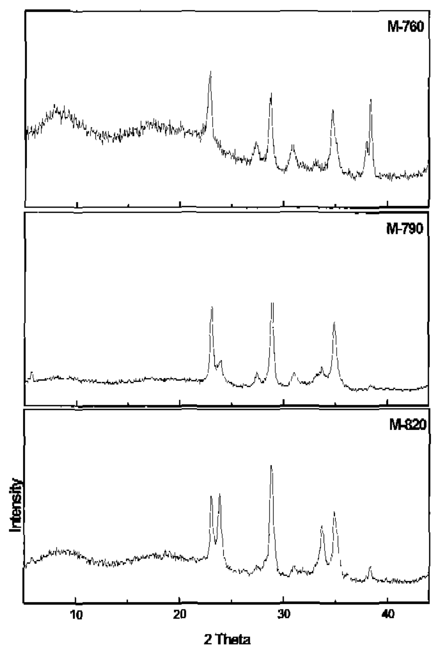


Fig.3 plots the XRD patterns of pre-annealed at various temperature - 760, 790 and 820 ℃ round wires which are prior to rolling.

of the wires made from pre-annealed and not pre-annealed precursor powders are shown in Fig. 4. The hardness of Bi-2212 orthorhombic phase was higher than that of Bi-2212 tetragonal phase. Although, softening annealing in the middle stage of drawing process might decrease work hardening, Bi-2212 orthorhombic phase was harder than Bi-2212 tetragonal phase.

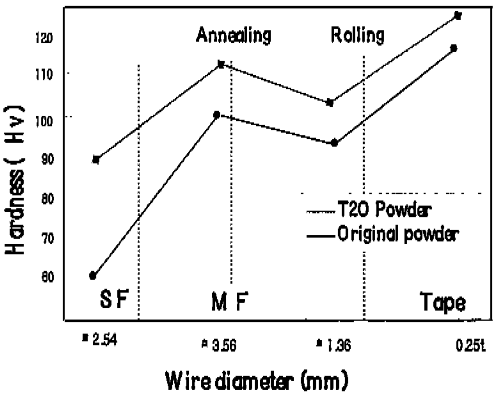
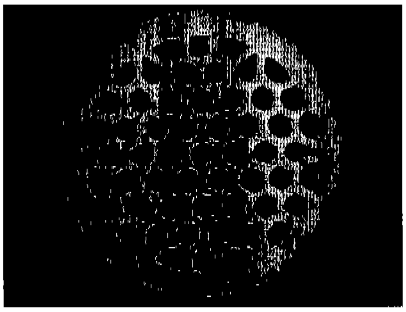
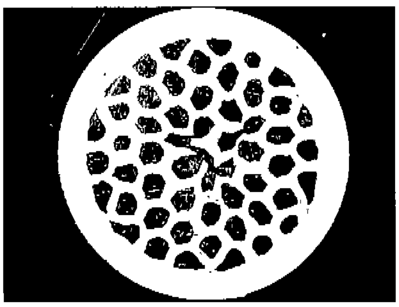


Fig. 4. Vicker's hardness of the wires that used pre-annealed precursor powder and used not pre-annealed precursor powder.

orthorhombic phase. Further, the filament break was appeared at the wire with Bi-2212 orthorhombic phase. These results are in accord with hardness test results in



(a) Tetragonal powder



(b) Orthorhombic powder

Fig. 5. shows the cross-section of 2 kinds of 55 filaments Bi-2223/Ag HTS wires with 3.55

Fig. 4. Hence, we can see that softening annealing is important to avoid the filament break when Bi-2212 orthorhombic phase is used.

The various heat treatment conditions of Bi-2223/Ag tapes are shown in Table 1. These specimens were heat treated by the combination of pre-annealing, first sintering and second sintering stages. Engineering critical current density (Je) properties of Bi-2223/Ag tapes show in Fig. 6.

The Je values of the tapes consisted of Bi-2212 orthorhombic phase are higher than those of Bi-2212 tetragonal. And the highest Je was 6500 A/cm2 at the tape using Bi-2212 orthorhombic phase which was slightly overheated at the first sintering process. It is considered that Bi-2212 orthorhombic phase promotes Bi-2223 formation and thus decreases second phases.

4. CONCLUSION

Bi-2212 phase was identified to transform from tetragonal to orthorhombic structure through the heat treatment at 760℃, 0.1% O_2 at pre-cursor powder and multi filamentary wire.

Second phases and Ca_2PbO_4 peaks could be decreased by transformation from tetragonal to orthorhombic Bi-2212 structure. To produce Bi-2223 conductor, frequent annealing was effective at low temperature because pre-annealing at precursor powder brought about decrease of workability. The highest Je was 6500 A/cm2 at the tape using Bi-2212 orthorhombic phase by introduced slightly over heating at 1st sintering process.

TABLE I THE VARIOUS HEAT TREATMENT CONDITIONS OF BI-2223/AG TAPES.

Symbol	Pre-annealing condition	Temp. of 1st sintering	Temp.of 2nd sintering
APHPH	Yes	High	High
NPHPH	No	High	High
APHPL	Yes	High	Low
NPHPL	No	High	Low
AOLPL	Yes	Over heat	Low
NOLPL	No	Over heat	Low

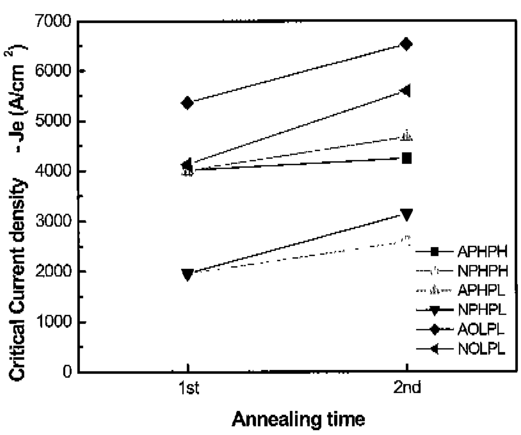


Fig. 6. Engineering critical current density (Je) properties of Bi-2223/Ag tapes.

ACKNOWLEDGMENT

This research was supported by a grant from Center for Applied Superconductivity Technology of the 21st Century Frontier R&D Program founded by The Ministry of Science and Technology, Republic of Korea.

EXAMPLE REFERENCES

[1] W. G. Wang, J. Horvat, B. Zeimetz, H. K. Liu, S. X. Dou Physica C 291, 1-7 (1997).
[2] J. Horvat, Y. C. Guo, B. Zeimetz, H. K. Liu, S. X. Dou, Physica C 300, 43-48 (1998).
[3] Hua Deng, Peiwen Hua, Wenquan Wang, Cheng Dong, Hong Chen, Fei Wu, Xiaohua Wang, Yiru Zhou, Guansen Yuan, Physica C, 339, 181-194 (2000).
[4] Y. C. Guo, J. Horvat, H. K. Liu, S. X. Dou Physica C, 300, 38-42 (1998).
[5] Rupich et al., United States Patent, US 6295716 B1 (2001).