

Effects of Cooling Rate on the Microstructures and Transport Properties of AgAu Sheathed Bi-2223 Tapes

Ma Xiaobo^{1,2}, Zhang Shengnan², Yu Zeming², Liu Guoqing², Jiao Lei², Zheng Hui-ling², Li Chengshan², Zhang Pingxiang^{1,2}, Li Jinshan¹

¹ State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China; ² Northwest Institute for Nonferrous Metal Research, Xi'an 710016, China

Abstract: Monofilament AgAu sheathed Bi-2223 tapes were fabricated by powder in tube (PIT) process. The influences of cooling rate during the second heat treatment process (HT2) on the phase composition, microstructures and transport properties of Bi-2223/AgAu tapes were investigated. Results show that after the HT2 process, the content of Pb-rich $\text{Pb}_3\text{Sr}_{2.5}\text{Bi}_{0.5}\text{Ca}_2\text{CuO}_y$ (3321) phase increases with the decreasing cooling rate, while the size of CuO phase particles becomes bigger. With the cooling rate decreasing from 600 °C/h by 1 °C/h, the critical current density J_c increases from 7 kA/cm² to the maximum value of 11.5 kA/cm², which increases by 64%. Meanwhile the current capacities in magnetic field of these Bi-2223/AgAu tapes have also been enhanced with slow cooling process, attributed to the improvements of both the intergrain connectivity and the flux pinning properties.

Key words: high temperature superconductor; (Bi, Pb)-2223/AgAu tapes; cooling rate; microstructure; critical current density

Since the first discovery of Bi-based superconductors in 1986, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (Bi-2223) has become one of the most promising high temperature superconductors (HTS) for practical applications under liquid nitrogen temperature (77 K), due to the high superconducting transformation temperature ($T_c \sim 110$ K) and high critical current density (J_c)^[1-3]. Recently, AgAu sheathed Bi-2223 has been recognized to be the best candidate for the fabrication of HTS current lead, considering the extremely low thermal conductivity of AgAu sheath^[4]. However, the phase evolution process of AgAu sheathed Bi-2223 tapes is different from that of Ag sheathed tapes attributed to the slower oxygen penetration rate of AgAu alloy^[5]. Nowadays, the obtained current capacity of AgAu sheathed tapes is still ~30% lower than that of Ag sheathed tapes^[6]. Therefore, it is quite necessary to study the phase evolution process in the AgAu sheathed tapes and to enhance their current capacity.

In Ag sheathed tapes, based on previous studies, it was reported that the microstructures, including the size of

secondary phase, texture structures and phase distribution of the ceramic core played an important role in the current transport properties. And the cooling process of heat treatment had a great influence on the microstructures of Bi-2223/Ag tapes, by varying the phase composition as well as particle sizes of different phases. In Bi-2223 tapes, secondary phases, such as $(\text{Ca,Sr})_2\text{CuO}_3$ (namely 2:1 AEC), CuO and $(\text{Ca,Sr})_{14}\text{Cu}_{24}\text{O}_{41}$ (namely 14:24 AEC) formed during the sintering process can be reserved during the cooling process. Meanwhile, precipitates of liquid phase at high temperatures tended to assemble at grain boundaries as intergrain weak links. These secondary phases may persist in the final product and block/break the current paths, thus diminishing the current-carrying capacity of the fully tapes^[7,8]. So it is crucial to tune the phase composition of secondary phases through the cooling process. A significant number of studies related to the effect of cooling on the transport properties and microstructures in the final processed tapes have been published previously^[9-13].

Received date: June 25, 2018

Foundation item: National Key Project of Magneto-Constrained Fusion Energy Development Program (2015GB115001)

Corresponding author: Zhang Pingxiang, Ph. D., Professor, Northwestern Polytechnical University and Northwest Institute for Nonferrous Metal Research, Xi'an 710016, P. R. China, Tel: 0086-29-86231079, E-mail: yequ198508@163.com

Copyright © 2019, Northwest Institute for Nonferrous Metal Research. Published by Science Press. All rights reserved.

Parrell et al.^[12] reported that slow cooling (<0.1 °C/min) in 7.5% O₂ atmosphere could increase the J_c (77 K, self-field) values by as much as 50% over the tapes cooled more quickly, and considerably sharpened the T_c transition, despite the decomposition of Bi-2223 phase at temperatures below the 2223 phase stability limit. Tetenbaum and Maroni^[14] discovered that slow cooling process could also lead to the increase of the oxygen content in Bi-2223 phase, which could contribute to the enhanced critical current density. Chen^[15] et al investigated the effect of cooling rate on the transport properties and microstructures after the first heat treatment. The results showed that the critical current density increases linearly with the cooling rate decreasing logarithmically due to the obvious optimization of both the Bi-2223 phase purity and on the connectivity between grains.

In the present study, aiming at the enhancement of current capacity in AgAu sheathed Bi-2223 tapes, the influences of cooling rate in the second heat treatment process on the phase composition, microstructures and transport properties of AgAu sheathed Bi-2223 tapes were discussed. The AgAu sheathed Bi-2223 tapes have been fabricated with the two-powder precursor powders and traditional powder in tube process. An obvious enhancement of J_c over 64% was obtained with the cooling rate of 1 °C/h.

1 Experiment

AgAu5wt% sheathed (Bi, Pb)-2223 mono-filamentary tapes were fabricated with the powder in tube (PIT) technique^[16], and the precursor powders with the nominal composition of Bi_{1.76}Pb_{0.34}Sr_{1.93}Ca_{2.02}Cu_{3.06}O_x were prepared by the two-powder process^[17] with the initial phase assemblage of the as-rolled tapes Bi-2212, Ca₂CuO₃ and CuO. Samples of as-rolled tapes with the length of 10 cm were then thermo-mechanically processed by three heat treatments (namely first heat treatment (HT1), second heat treatment (HT2) and third heat treatment (HT3), and an intermediate rolling step between HT1 and HT2 to develop a dense and aligned Bi-2223 phase structure. The HT2 process was performed at 826 °C for 78 h in flowing 7.5% O₂/Ar atmosphere. The samples were then cooled from 826 °C to 800 °C under electronic furnace programmer control with the cooling rates of 600 (quench in air), 100 (furnace cooling), 6, 2, 1 and 0.5 °C/h. Below 800 °C, the samples were furnace-cooled with the cooling rate of ~100 °C/h. The HT3 process was performed at 780 °C for 18 h in flowing 7.5 % O₂/Ar atmosphere. The final cross section dimensions of all these tapes were ~0.33×4.76 mm.

Polycrystalline X-ray diffraction (XRD) patterns of tapes were taken on a X-ray diffractometer (Bruker D8 Advance) with Cu-K α radiation. XRD analysis was performed by peeling off the Ag-Au sheath from one side and exposing the flat ceramic core surface to the X-ray beam. The Bi-2223 and Bi-2212 phase volume fractions of powders were calculated based on the intensities of some specific peaks on X-ray

diffraction patterns, namely,

$$V_{2223}(\%) = I_{2223(0010)} / [I_{2223(0010)} + I_{2212(008)}] \times 100\% \quad (1)$$

$$V_{2212}(\%) = I_{2212(008)} / [I_{2223(0010)} + I_{2212(008)}] \times 100\% \quad (2)$$

where, $I_{2223(0010)}$ and $I_{2212(008)}$ are the intensities of (0010) peak of Bi-2223 and (008) peak of Bi-2212, respectively. Microstructures of the final tapes were examined by scanning electron microscopy (SEM). Polished samples in transverse view were observed using backscattered electrons with a JEOL 6400 SEM. Chemical compositional analysis was performed by Inca-X-Stream energy-dispersive X-ray spectroscopy (EDX). The critical current (I_c) at 77 K, 0 T was measured using a standard four-probe DC method with the criterion of 1 μ V/cm. Critical current density J_c was calculated as $J_c = I_c/A$, where A is the cross section area of superconducting core. The critical currents in magnetic field were measured at 77 K in the magnetic field from 0 T to 0.6 T, both parallel and perpendicular to the rolling plane of the tape.

2 Results and Discussion

X-ray diffraction patterns of the samples with different cooling rates of 1, 6, 100 and 600 °C/h are shown in Fig.1. The patterns have been plotted into logarithmic coordinates to show the characterized peaks of secondary phases clearly. The existences of secondary phases including Bi₂Sr₂CaCu₂O_{8+ δ} (2212), (Ca, Sr)CuO₂ (1:1 AEC) and CuO can all be clearly observed as marked by different symbols. Based on the calculation by Eq.(2), the contents of 2212 phase are approximately 5% in different tapes regardless of the cooling rate. Meanwhile, under different cooling rates, the contents of both 1:1 AEC and CuO phases remain basically the same. While in the tapes with large cooling rate (air-quenched and 100 °C/h), there is almost no Pb-rich Pb₃Sr_{2.5}Bi_{0.5}Ca₂CuO_y,

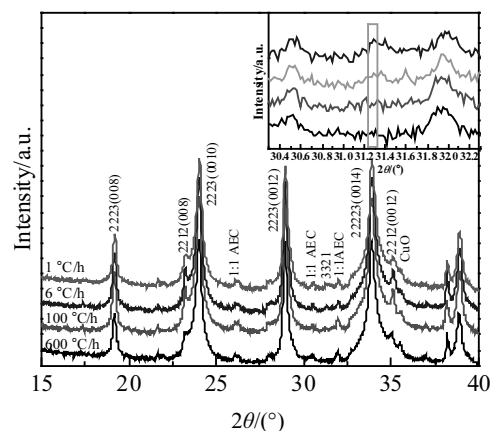


Fig.1 X-ray diffraction patterns of Bi-2223 tapes with the cooling rate of 1, 6, 100 and 600 °C/h (diffraction peaks of 3321 phase at 31.3° are zoomed in the inset)

(3321) phase. However, 3321 phase begins to appear in the slow cooled tapes (1 and 6 °C/h). And the content of 3321 phase increases with decreasing cooling rate, as shown in the inset at $2\theta \approx 31.3^\circ$.

Backscattered electron images of the cross section of Bi-2223 tapes with different cooling rates are shown in Fig.2. It is known that different phases can be distinguished as contrast in backscattering electron images. Therefore, it can be observed that in all these tapes, Bi-2223 grains align parallel to the tape surface as light gray matrix. Besides, there exist three different kinds of secondary phases, shown as black and dark gray particles and white sheets. All the phases in the images have been carefully examined with EDX. And it can be observed that with different cooling rates, AEC phase as black particles and CuO as dark gray particles (as marked by arrows) exist in all the tapes. And with the decrease of cooling rate, the particle size of CuO increases obviously. It is because CuO phase is precipitated from the liquid phase during the high temperature heat treatment. Thus when the cooling rate is slow, it is very beneficial for the formation and growth of CuO particles^[15]. In Fig.2a and 2b, no Pb-rich $\text{Pb}_3\text{Sr}_{2.5}\text{Bi}_{0.5}\text{-Ca}_2\text{CuO}_y$ (3321) phase can be observed in the samples with slow rate of 1 °C/h and 6 °C/h. However, from XRD patter (Fig.1), the content of 3321 phase increases with the decrease of cooling rate. This is probably because in the slowly cooled samples, although 3321 phase has precipitated from liquid, the particle size is too small to be observed under this magnification. As shown in Fig.2c and 2d, there is a large content of white un-crystallized liquid phase. It is because the cooling rate is too large, and thus the liquid phase is unable to form at the high temperature to crystallize.

Fig.3 shows the J_c value (77 K, self-field) as a function of cooling rate from 0.5 °C/h to 600 °C/h. It can be noted that the J_c values increase from 7 kA/cm² of the 600 °C/h cooled tape to the maximum value of 11.5 kA/cm², which is obtained with the cooling rate of 1 °C/h. Then with the further decrease of cooling rate to 0.5 °C/h, the current density greatly decreases to 7.6 kA/cm². The Bi-2223 volume fraction of powder close to AgAu-sheath was calculated by Eq.(1). The obtained Bi-2223 volume fraction decreases from 93% for 1 °C/h cooled tape to 85% when the cooling rate is lower than 1 °C/h. Considering that the Ag-superconductor boundary is the high current capacity area, the decomposition of the Bi-2223 phase in this area is the reason for the obvious J_c decreasing at the cooling rate of 0.5 °C/h. It can be concluded that the optimized cooling rate for our AgAu sheathed Bi-2223 tapes is 1 °C/h from 826 °C to 800 °C.

Generally speaking, there are two factors which can affect the current capacity of Bi-2223 tapes, namely the intergrain connections and flux pinning properties. In order to understand the reason for the enhancement of J_c in 1 °C/h cooled tapes compared to the tapes with large cooling rate, critical currents were measured for 1, 6 and 100 °C/h cooled tapes under the magnetic field of 0 to 0.6 T. Fig.4 shows both the critical current density J_c (77K, 1μV/cm) values and normalized $J_c/J_c(0)$ values as functions of magnetic field applied parallel to the tape surface of samples cooled at 100, 6, and 1 °C/h. It can be observed that within the entire applied magnetic field region, the maximum values are all obtained in the tape with 1 °C/h cooling rate, and the decreases of normalized J_c values with magnetic field is slower for the 1 °C/h cooled tapes, which both suggest that the intergrain

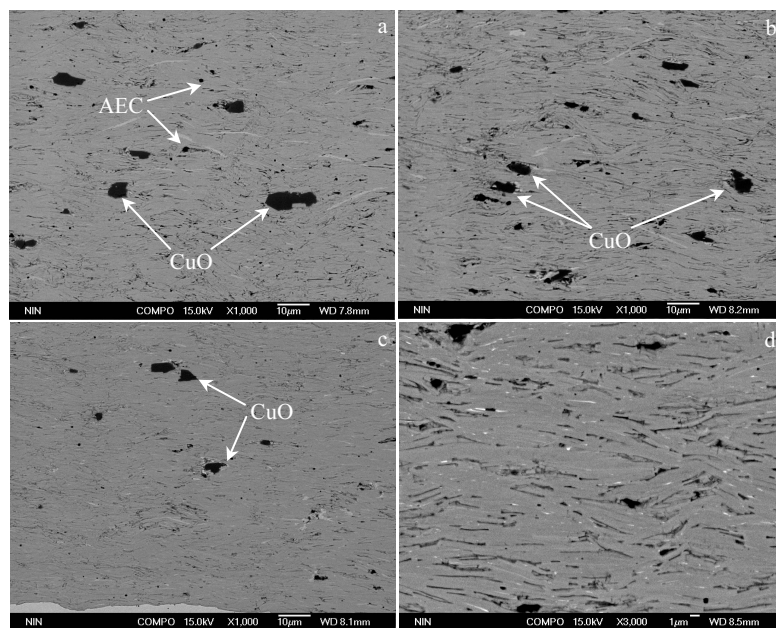


Fig.2 Backscattered electron images of Bi-2223/AgAu tapes with the cooling rate of 1 °C/h (a), 6 °C/h (b), 100 °C/h (c), and 600 °C/h (d)

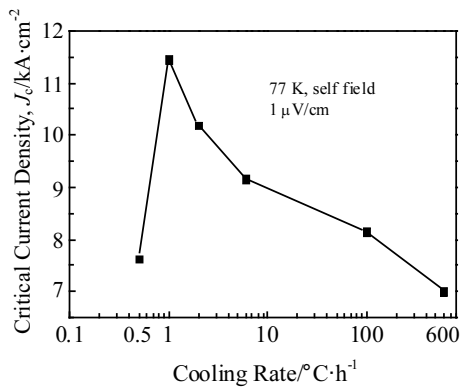


Fig.3 J_c (77 K, self-field) as the function of cooling rate (the temperature range is from 826 °C to 800 °C)

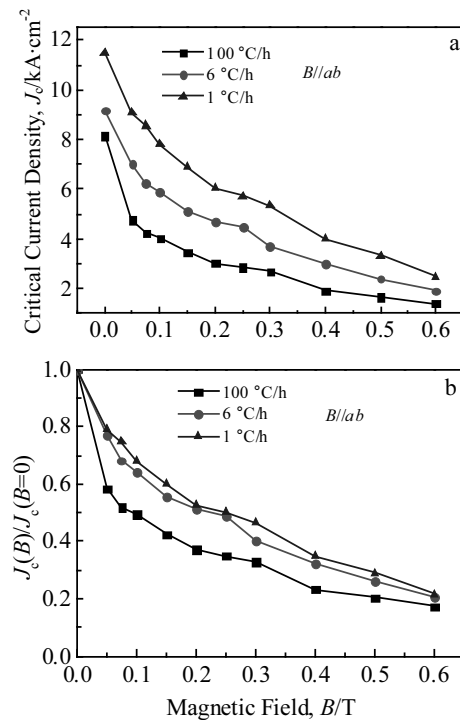


Fig.4 Critical current density as a function of magnetic field applied parallel to the ab plane of Bi-2223 tapes with cooling rate of 1, 6 and 100 °C/h (a) and normalized J_c value as a function of magnetic field (b)

connections has been greatly enhanced with the decrease of cooling rate.

Fig.5 shows the critical current density and normalized $J_c/J_c(0)$ value in magnetic field applied parallel to the nominal direction of the tape surface. The slowly cooled samples exhibit better in-field J_c retention at all fields applied parallel to the nominal direction, just as they do at fields applied parallel to the ab plane, which suggests the enhancement of flux pinning properties with slow cooling process. Based on the XRD and SEM results, the amount and size of second

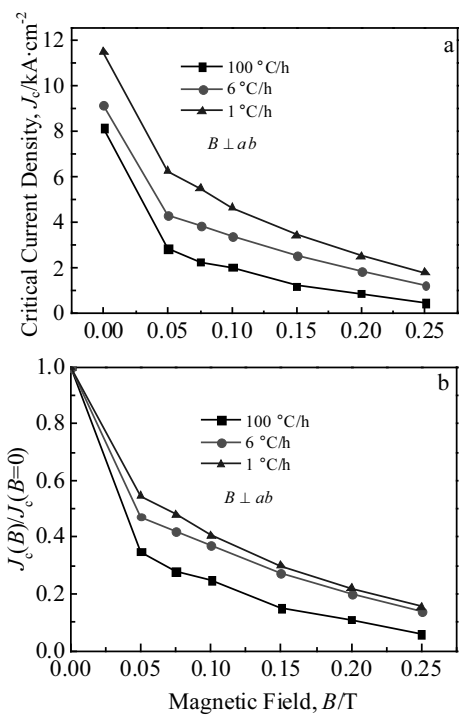


Fig.5 Critical current density as a function of magnetic field applied parallel to the nominal direction of the tape surface (a) and normalized J_c value as a function of magnetic field (b)

phase particles, especially CuO, slightly increase with the decreasing cooling rate. Thus the reduced volume fraction of second phase cannot be the reason for the observed I_c benefits of slow cooling. Since the formation of the Bi-2223 phase always involves liquid phases^[18-21], the residual liquid phase at grain boundaries is considered as intergrain weak links for the current transport process. As shown in Fig.2d, in the tapes with larger cooling rate, there is no enough time for these liquid phase to crystallize. While, when the cooling rate is slow, crystallized 3321 phase can precipitate from these liquid phases, which disperse precipitates uniformly at grain boundaries and is not only beneficial to the intergrain connections, but also work as flux pinning centers to enhance the flux pinning properties of Bi-2223 tapes. Therefore, the current capacity of our AgAu sheathed Bi-2223 tapes has been greatly enhanced both under self field and magnetic field.

Besides, we have also study the effects of slow cooling rate on the current transport properties of 37 filaments AgAu sheathed Bi-2223 tapes. The enhanced I_c values from 112 A for 100 °C/h cooled tape to 144 A for 1 °C/h cooled tape, corresponding to the 27% J_c increase from 11.7 kA·cm⁻² to 14.8 kA·cm⁻² suggest the effect of slow cooling process on the enhancement of superconducting transport properties of multifilamentary AgAu sheathed tapes.

3 Conclusions

1) With the decrease of cooling rate, although the CuO particle size slightly increases, which will affect the texture structure of Bi-2223 alignment, the precipitates of 3321 phase are greatly beneficial to the intergrain connections.

2) The J_c values both under self-field and in low magnetic field (parallel to the ab plane and the nominal direction of tape surface) have been obviously enhanced. Attributed to the good grain connectivity and enhanced flux pinning force, the maximum J_c value of 11.5 kA/cm² is obtained at the cooling rate of 1°C for mono-filamentary tapes.

References

- Nassi M. *Supercond Sci Technol*[J], 2000, 13: 460
- Sato K, Kato T, Hkura K O et al. *Supercond Sci Technol*[J], 2000, 13: 18
- Paul W, Lakner M, Rhyner J et al. *Supercond Sci Technol*[J], 1997, 10: 914
- Fujishiro H, Ikebe M, Noto K et al. *IEEE Trans Appl Supercond*[J], 1994, 30: 1645
- Grasso G, Jeremie A, Flukiger R. *Supercond Sci Technol*[J], 1995, 8: 827
- Yi H P, Song X H, Liu L et al. *Physica C*[J], 2005, 426-431: 1176
- Holesinger T G, Bingert J F, Willis J O et al. *IEEE Trans Appl Supercond*[J], 2002, 9(2): 2440
- Chen X P, Grivel J C, Li M Y et al. *Physica C*[J], 2004, 406(3-4): 176
- Sang S O, Kubota T, Osamura K. *Physica C*[J], 1990, 171(3-4): 265
- Huang Y B, Fuente G F, Larrea A et al. *Supercond Sci Technol*[J], 1994, 7: 759
- Yoshida K, Sano Y, Tommi Y. *Supercond Sci Technol*[J], 1995, 8: 329
- Parrell J A, Larbalestier D C, Riley G N et al. *Appl Phys Lett*[J], 1996, 69: 2915
- Lelovic M, Deis T, Eror N G et al. *Supercond Sci Technol*[J], 1996, 9: 965
- Tetenbaum M, Maroni V A. *Physica C*[J], 1996, 260(1-2): 71
- Chen X P, Li M Y, Qu T M. *Supercond Sci Technol*[J], 2003, 16: 1162
- Yoo J M, Chung H S, Ko J W et al. *Physica C*[J], 1996, 267(1-2): 53
- Dorris S E, Prorok B C, Lanagan M T et al. *Physica C*[J], 1993, 212(1-2): 66
- Sung Y S, Hellstrom E E. *Physica C*[J], 1995, 253(1-2): 79
- Yamada Y, Obst B, Flukiger R. *Supercond Sci Technol*[J], 1991, 4: 165
- Chen F H, Koo H S, Tseng T Y. *Appl Phys Lett*[J], 1991, 58(6): 637
- Lanagan M T, Kupperman D S, Yaconi G A et al. *IEEE Trans Appl Supercond*[J], 1995, 5(2): 1475

降温速率对 Bi-2223/AgAu 带材微观结构和传输性能的影响

马小波^{1,2}, 张胜楠², 于泽明², 刘国庆², 焦磊², 郑会玲², 李成山², 张平祥^{1,2}, 李金山¹

(1. 西北工业大学 凝固技术国家重点实验室, 陕西 西安 710072)

(2. 西北有色金属研究院, 陕西 西安 710016)

摘要: 采用 PIT 工艺制备了单芯 Bi-2223/AgAu 带材, 系统地研究了第二次热处理阶段 (HT2) 降温速率对带材相组成、微观结构和传输性能的影响。结果表明: 随着降温速率的减小, 富铅相 3321 不断增加, CuO 颗粒尺寸逐渐增大。当冷却速率从 600 °C/h 减小到 1 °C/h 时, 临界电流密度 J_c 从 7 kA/cm² 增加到 11.5 kA/cm², 增加了 64%。由于晶间连接性能和磁通钉扎性能的提高, 在较低的降温速率下, Bi-2223/AgAu 带材在磁场下的临界电流密度也得到了提高。

关键词: 高温超导; (Bi, Pb)-2223/AgAu 带材; 降温速率; 微观结构; 临界电流密度

作者简介: 马小波, 男, 1985 年生, 博士生, 西北工业大学凝固技术国家重点实验室, 陕西 西安 710072, 电话: 029-86231079, E-mail: yequ198508@163.com