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Critical current enhancement in Bi-2223/Ag superconducting tapes by controlling its first sintering process

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ABSTRACT

Microstructural evolution of the Bi-2223 phase, liquid phase and secondary phase in the first sintering process has been studied by means of XRD and SEM/EDS. Experiments show that the first sintering temperature and time have a great influence on the Bi-2223 phase formation. The cooling rate after the first sintering process determines the type and grain size of the secondary phases, which in turn decides the critical current of the fully reacted tapes. The fast cooled sample contains a few secondary phase particles with very small size, whereas the slow cooled sample produces large CuO particles. The $(Ca,Sr)_2CuO_3$ and $(Ca,Sr)_{14}Cu_{24}O_{41}$ phases are easy to deform, while CuO phase particle has a high hardness and is difficult to deform during uniaxial press. The critical current is largely improved by controlling the cooling rate of the first sintering process.

1. Introduction

Silver-sheathed Bi-2223 (Bi-2223/Ag) superconducting tapes are the most applicable high-T_c tapes for 77 K usage at the present stage owing to their capability of carrying large currents and a relatively simple fabrication process ("powder-in-tube" technique) for long-length tapes. Currently, Bi-2223/Ag superconducting tapes are applied to various devices such as power transmission cables, magnets, motors and generators. For realization of such applications, much effort has been made in order to further improve the critical current density of the Bi-2223/Ag tapes [1–5]. It is widely accepted that one important factor for the successful control of the phase formation and the microstructure is the first sintering process of the tapes, which seems to be a critical step for the formation of a desirable final structure [5–9]. During the first sintering process, a majority of the precursor powder is converted into the superconducting Bi-2223 phase. At the same time, some non-superconducting secondary phases, such as $(Ca,Sr)_2CuO_3$ (2:1), CuO and $(Ca,Sr)_{14}Cu_{24}O_{41}$ (14:24) are also formed, which often grow as non-plate shaped crystals, and remain in the final product, thus degrading the connectivity of the Bi-2223 microstructure of the fully reacted tapes [10,11]. Therefore it is crucial to control the size and amount of the secondary phase particles produced in the first sintering process.

Low oxygen partial pressure and low annealing temperature seem preferable for the control of the formation of the secondary phases [11]. It was reported in Refs. [8,9] that the amount and size of the secondary phase particles produced in the first sintering process could be optimized by controlling the sintering parameters and oxygen partial pressure, tapes with the lowest amount and minimum size of secondary phase produced in the first sintering process will obtain the best performance of the fully reacted tapes. On the other hand, the cooling rate after the first heat treatment also has a large effect on the critical current density and filament microstructure [12].

The first sintering process of the Bi-2223/Ag tapes is a complex process that is very sensitive to parameters, such as temperature, time, oxygen partial pressure and cooling rate. However, it is still not well understood how to obtain a best critical current of the fully reacted tapes by controlling the first sintering process.

In this work, we try to control the evolution of the secondary phases in the first sintering process for improving the critical current of Bi-2223/Ag tapes. This means that the tapes will be sintered by controlling the temperature, time and cooling rate during the first step. In the following steps, the tapes will be subjected to the same heat treatment under oxygen partial pressure. The influence of the evolution information on the critical current of the fully reacted tapes was discussed. The emphasis is to improve the tape

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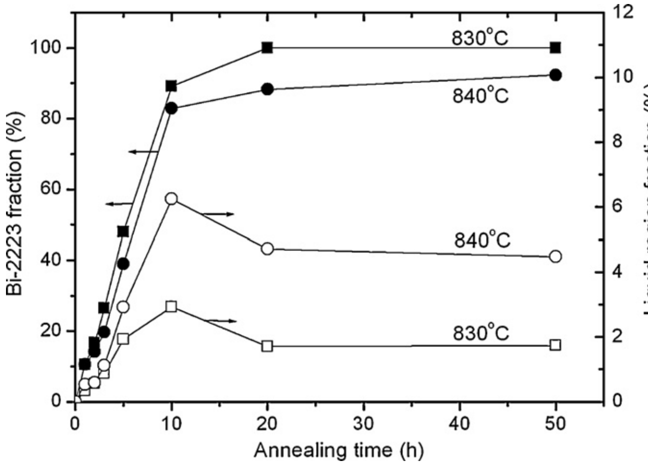

Fig. 1. Area fraction of quenched liquid regions (determined by SEM and image analysis) and Bi-2223 fraction as a function of annealing time.

performance by controlling the secondary phases evolution during the first sintering process.

2. Experimental details

The nominal composition of the precursor powder used in the tapes is $Bi_{1.8}Pb_{0.33}Sr_{1.87}Ca_{2.0}Cu_{3.0}O_y$. The initial phase assemblage of the green tape is Bi-2212, Ca_2PbO_4, $Pb_3Sr_{2.5}Bi_{0.5}Ca_2CuO_y$ (3321) and 14:24. The Bi-2223/Ag tapes was prepared by the standard industrial "powder-in-tube" (PIT) technique, samples of the mono-filamentary tape used in the experiments are typically 2.5 mm wide, 0.20 mm thick and ~50 mm long. The samples were sintered at 830 and 840 °C in the time range from 1 to 50 h, and then quenched in air.

X-ray diffraction (XRD) was carried out using CuKa radiation on the flat surface of tape samples after peeling away the outer layer of Ag. The volume fraction of the Bi-2223 phase formed in the core of the tape was calculated by taking the ratio of the (0 0 10) peak intensity of Bi-2223, to the sum of the (0 0 8) peak intensity of Bi-2212 and the (0 0 10) peak intensity of Bi-2223. The analysis of microstructure and composition was performed on transverse sections of the samples. SEM/EDS images were obtained on a Leo-1530 SEM equipped with an Oxford energy dispersive spectroscopy system in the backscattered electron (BSE) imaging mode. The area fraction of the liquid regions was determined by using Adobe Photoshop software. Measurements were averaged over at least two micrograph areas for each sample.

After the first sintering, samples were uniaxially pressed at ~1.5 GPa. All sintering process were performed in 8.5% O_2/balance N_2 atmosphere.

61-filamentary tapes (typically 4.5 mm wide, 0.20 mm thick) were used to study the effect of the cooling rate after the first sintering process on the final tape performance. The thermomechanical process of the multi-filamentary tapes is same as that of the mono-filamentary tapes.

The critical current was measured at 77 K by the standard four-probe technique with a criterion of 1 $\mu V\,cm^{-1}$.

3. Results and discussion

Fig. 1 shows the area fraction of quenched liquid regions and Bi-2223 fraction as a function of annealing time. It can be clearly seen that the development of the Bi-2223 phases at different sintering temperatures has the similar trend, where the Bi-2212 to Bi-2223 transformation is faster during the initial 10 h sintering period, after sintering for 10 h, the transformation rate of Bi-2223 is almost saturated. Samples treated at 830 °C have faster formation speed than that of being treated at 840 °C. Meanwhile, the evolution of the liquid phase fraction during the sintering shows an interesting feature. During the first 10 h, its volume fraction increases with the sintering time and reaches a maximum at 10 h and then slowly decreases, which is in good agreement with the results obtained by Liu et al. [7] and Giannini et al. [13]. We ascribe this to the fact that Bi-2212 phase, which is the main source of liquid phase, decreases rapidly during the fast formation of Bi-2223 during the first sintering process [14]. After 10 h sintering, the formation rate of the liquid phase can no more compete with its consumption rate and thus the global liquid phase volume decreases.

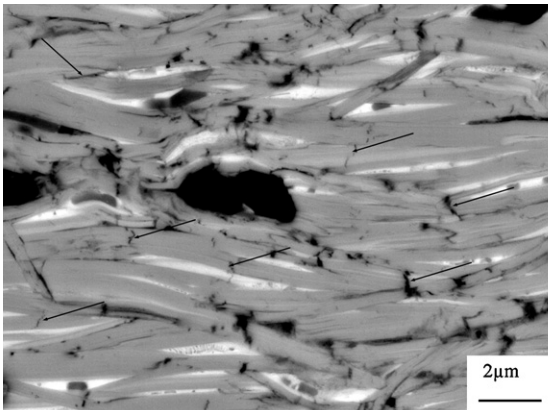

Fig. 2. SEM micrographs of samples after an intermediate press. Arrows indicate the cracks.

Based on the above findings, two time ranges can be defined in Fig. 1. In the first range (0–10 h), the volume fraction of both Bi-2223 and liquid phase increase sharply; in the second range (beyond 10 h), the variations are much more gradual. This is because all the liquid regions are completely enclosed by Bi-2223 platelets after 10 h or more, which will decrease the formation speed of Bi-2223 phase [14,15]. Thus, the intermediate mechanical deformation is needed at the time of 10 h sintering. Fig. 2 shows the effect of intermediate uniaxial pressing on the sample sintered at 840 °C for 10 h. As can be seen clearly, there are many cracks introduced through the deformation. As a consequence, during the subsequent annealing stages, the cracks which crossed the Bi-2223 platelets will allow the liquid regions receive the feed material from Bi-2212 and secondary phases, thus promoting the formation speed of Bi-2223 phase.

It is therefore deduced that 10 h is the critical point during the first sintering process of Bi-2223/Ag tapes. Furthermore, the specimens treated with this particular length of time had the lowest amount and minimum size of secondary phases [9]. Based on this understanding, we select 10 h as the first sintering time.

In order to explore the effect of the cooling rate after the first sintering on the microstructure of the tapes, samples were sintered at 840 °C for 10 h and then cooled at three different rates: quenched in air, 100 °C/h, and 3 °C/h. SEM images of the transversal microstructures of samples with different cooling rates are shown in Fig. 3. It is clearly observed that fast cooled (quenched in air) sample contains a few secondary phase particles with very small size. For the slowly cooled (3 °C/h) sample, however, there are more non-superconducting secondary phase particles, particularly the CuO phase particles, which appear with a large size.

The appearance of the large CuO phase particles in the slowly cooled sample shows a significant dependence on cooling rate. As shown in Fig. 3, there is a clear trend that the volume fraction of total secondary phase particles in the microstructure increases with decreasing cooling rate.

After the first sintering process, mechanical deformation steps are needed to densify and align the Bi-2223 phase. In order to check the effect of mechanical deformation on the secondary phase particles, several pieces of tapes have been treated at 840 °C for 10 h and cooled down at 100 °C/h. After this treatment, Samples were uniaxially pressed. Fig. 4 shows the SEM backscattered images of typical secondary phases after intermediate pressing. In these micrographs three major secondary phases are evident, which are CuO phase (Fig. 4(a)), 14:24 phase (Fig. 4(b)) and 2:1 phase (Fig. 4(c)), respectively. It can be obviously seen that the appearance of the secondary

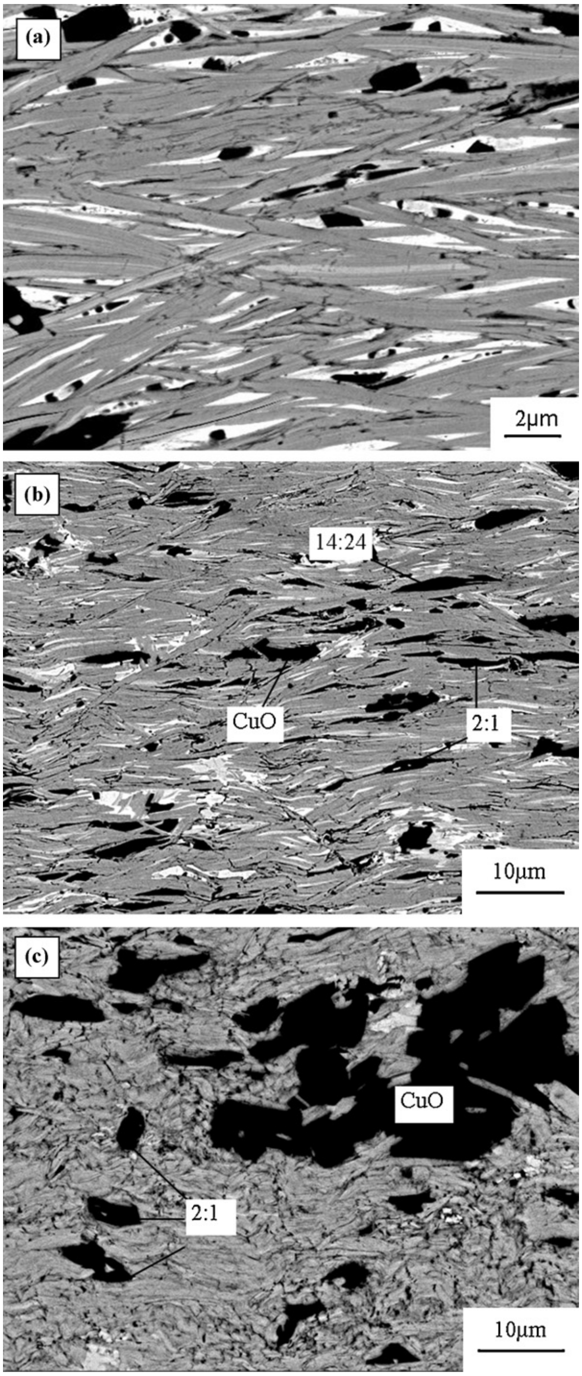

Fig. 3. SEM micrographs of samples sintering at 840 °C for 10 h and cooled at (a) Quenched, (b) 100 °C/h and (c) 3 °C/h.

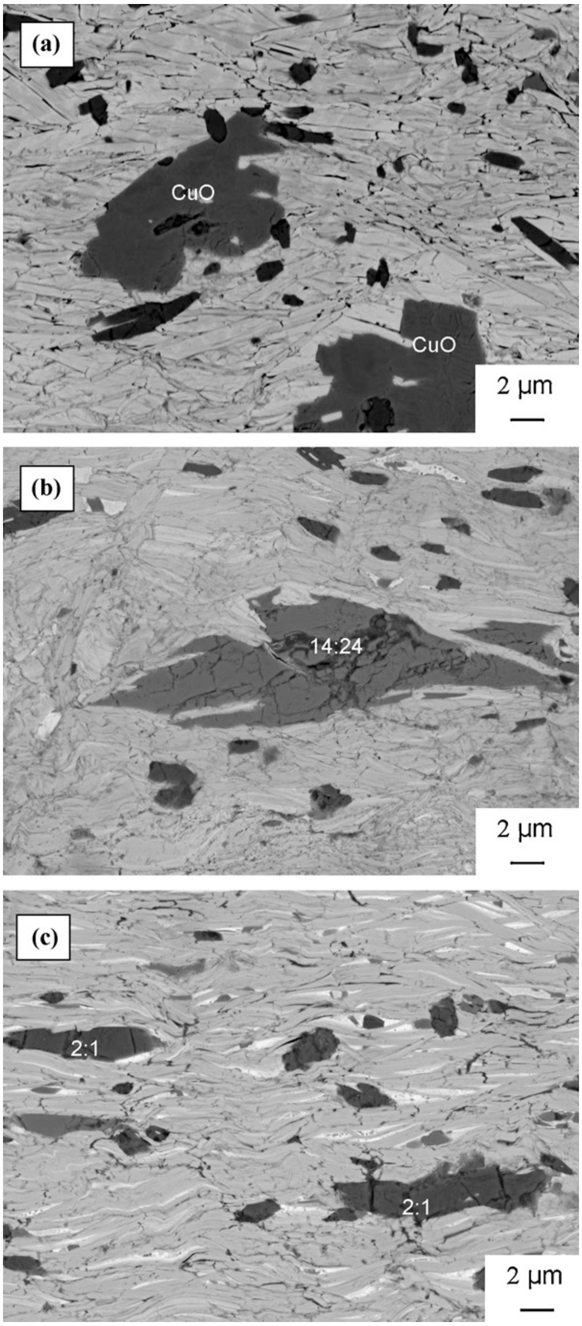

Fig. 4. SEM micrographs of typical secondary phases (a) CuO, (b) 14:24 and (c) 2:1 after intermediate pressing.

phases after the uniaxial pressing is very different. The 14:24 particles are obviously broken, and the 2:1 particles are partially broken. For the CuO particles, however, there is no any deformation after the pressing. This difference in appearance of secondary phase particles suggests that the CuO particles are the hardest, while 14:24 and 2:1 phase particles are easy to deform.

The development of the large non-plate shaped secondary phase particles will cause damage to some of the fully formed Bi-2223 grain colonies during subsequent mechanical deformation [10]. One would therefore expect that the particle size of the secondary phases is greatly reduced before the intermediate deformation. This is especially true if the cooling rate is very fast after the first sintering. As shown in Fig. 3(a), the fast cooling is effective in reducing the amount and size of secondary phase particles, especially in reducing the large CuO particles.

In order to study the effect of the cooling rate after the first sintering on the critical current of the tapes, 61-filament tapes were sintered at temperatures between 820 and 840 °C for 10 h, followed by normal cooling (100 °C/h) and quenched in air, respectively. The critical currents of the samples after the first heat treatment are shown in Fig. 5. We note that, independent of the height of the first sintering temperature, the critical current of the quenched samples (at different sintering temperatures) is obviously lower than that of normal cooling samples. We ascribe this to the following aspects: during the normal cooling process, the Bi-2201 phase formed at high temperature converts to Bi-2212 and Bi-2223 phase [16,17], which improves the intergranular connectivity. On the other hand,

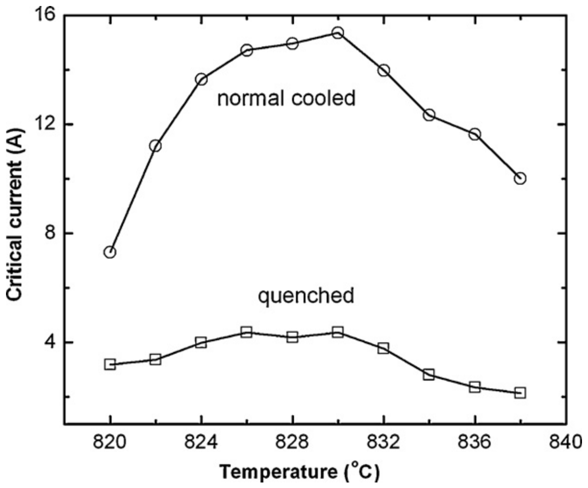

Fig. 5. Critical current vs. sintering temperature in the first sintering process.

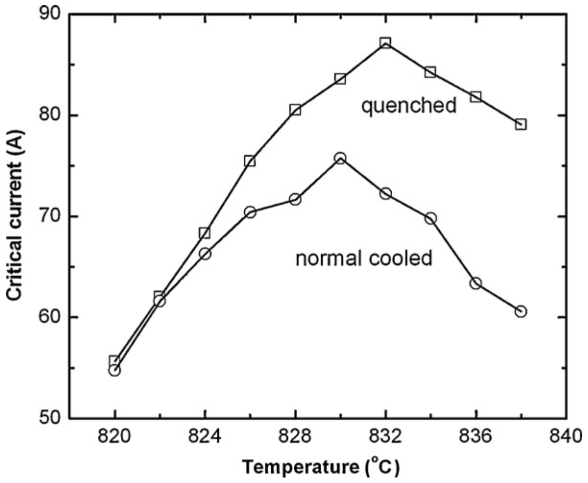

Fig. 6. Critical current of the fully reacted tapes with different sintering temperature and cooling rate in the first sintering process.

the slower cooling rate often results in a change in the oxygen content and cation stoichiometry of Bi-2223 phase, which increases the irreversibility field [12], and thereby improves the overall critical current of the tapes.

After the first sintering process, all samples were put through the same thermomechanical treatment. Fig. 6 shows the critical current of the fully reacted tapes with different sintering temperature and different cooling rate in the first sintering process. It is striking to note that the critical current of the tapes with intermediate quench is significantly improved. Clearly, samples with intermediate quench after the first sintering produced much higher critical current overall, with the maximum value of 87.2 A (The critical current density (J_c) is about 32.9 KA/cm^2). For the samples normally cooled after the first sintering, however, the critical current reached a maximum of only 75.7 A. Our results indicate that the cooling rate after the first sintering process has a key influence on the critical current of the fully reacted tapes. The above results suggest that large secondary phases formed during the first sintering process will destroy the connectivity of polycrystalline core, and thus decrease the critical current of the tapes.

4. Conclusions

The present data demonstrate that the critical current of the fully reacted tapes could be largely improved by controlling the cooling rate in the first sintering process of Bi-2223/Ag tapes.

It was found that dwelling time of 10 h is the critical point during the first sintering process of Bi-2223/Ag tapes, after which Bi-2223 phase formation rate is almost saturated. The cooling rate after the first sintering process determines the type and grain size of the secondary phases, which in turn decides the critical current of the fully reacted tapes. The fast cooled sample contains a few secondary phase particles with very small size, whereas the slow cooled sample produces large CuO particles. The $(Ca,Sr)_2CuO_3$ and $(Ca,Sr)_{14}Cu_{24}O_{41}$ phases are easy to deform, while CuO particle has a high hardness and is difficult to deform when pressed. Therefore, for the first sintering process of the Bi-2223/Ag tapes, it would be an advantage conducting tests to ensure the cooling rate after the first sintering is great enough to obtain the best performance of the fully reacted tapes.

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References

[1] A.P. Malozemoff, D.T. Verebelyi, S. Fleshler, D. Aized, D. Yu, Physica C 386 (2003) 424.
[2] X.P. Chen, J.-C. Grivel, M.Y. Li, Q. Liu, Z. Han, N.H. Andersen, J. Homeyer, Physica C 407 (2004) 147.
[3] T.M. Qu, Z.R. Han, Flükiger Phys. C 444 (2006) 71.
[4] N. Ayai, M. Kikuchi, K. Yamazaki, S. Kobayashi, S. Yamade, E. Ueno, J. Fujikami, T. Kato, K. Hayashi, K. Sato, R. Hata, J. Iihara, K. Yamaguchi, J. Shimoyama, IEEE Trans. Appl. Supercond. 17 (2007) 3075.
[5] X.D. Su, Supercond Sci. Technol. 20 (2007) 955.
[6] B. Fischer, T. Arndt, J. Gierl, H. Krauth, M. Munz, A. Szulczyk, M. Leghissa, H.-W. Neumuller, IEEE Trans. Appl. Supercond. 11 (2001) 3261.
[7] Y.L. Liu, J.-C. Grivel, W.G. Wang, H.F. Poulsen, Supercond. Sci. Technol. 14 (2001) 929.
[8] R.M. Baurceanu, V.A. Maroni, N.N. Merchant, A.K. Fischer, M.J. McNallan, R.D. Parrella, Supercond. Sci. Technol. 15 (2002) 1167.
[9] X.P. Chen, M.Y. Li, Q. Liu, Z. Han, Physica C 469 (2009) 116.
[10] T.G. Holesinger, J.F. Bingert, J.O. Willis, Q. Li, R.D. Parrella, M.D. Teplitsky, M.W. Rupich, G.N. Riley Jr., IEEE Trans. Appl. Supercond. 9 (1999) 2440.
[11] J.S. Luo, N. Merchant, E.J. Escorcia-Aparicio, V.A. Maroni, B.S. Tani, W.L. Carter, G.N. Riley Jr., J. Mater. Res. 9 (1994) 3059.
[12] J.A. Parrell, D.C. Larbalestier, S.E. Dorris, IEEE Trans. Appl. Supercond. 5 (1995) 1275.
[13] E. Giannini, E. Bellingeri, R. Passerini, R. Flükiger, Physica C 315 (1999) 185.
[14] X.P. Chen, J.-C. Grivel, M.Y. Li, T.M. Qu, Z. Han, Q. Liu, N.H. Andersen, J. Mater. Sci. 40 (2005) 5721.
[15] T.M. Qu, X.P. Yang, C. Gu, X.P. Chen, Z. Han, P. Zeng, Physica C 468 (2008) 1767.
[16] X.P. Chen, M.Y. Li, T.M. Qu, Q. Liu, Z. Han, Supercond. Sci. Technol. 16 (2003) 1162.
[17] W.G. Wang, J. Horvat, B. Zeimetz, H.K. Liu, S.X. Dou, Physica C 291 (1997) 1.