Effects of intermediate annealing on the microstructure and transport properties of Bi-2223 wires and tapes

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Abstract. Monofilament and 37-filamentary Bi-2223 tapes were fabricated by powder in tube (PIT) process. And the mono-filamentary wires were drawn from ø12mm to hexagon 1.51 mm with one and three times intermediate annealing, respectively. The influences of different intermediate annealing times on the core density, morphology and transport properties of Bi-2223 wires and tapes were systematically investigated. It was noticed that the density and the Vickers micro-hardness values of superconducting core on the cross-section of one time annealing wires were higher than those of three times annealing wires. Meanwhile, it was observed that the Ag/oxide core interfaces of the wire with one time annealing were more smooth than those of the three times annealing wire. With the intermediate annealing time decreasing from three to one, the critical current density \( J_c \) increased from 17.9 kA/cm\(^2\) to 20.5 kA/cm\(^2\). And the enhancement of \( Jc-B \) properties suggests the improvement of intergrain connections due to the increasing core density. Meanwhile one time annealing procedure was used to Ag-Au sheathed tape, \( J_c \) reached 16.3 kA/cm\(^2\), this value was also higher than those traditional wires in our previous experiments, which suggests that the decreasing of annealing times during drawing process is also effective in AgAu sheath tapes for the enhancement of current capacity.

1. Introduction
Since the first discovery of Bi-based superconductors in 1986, Bi\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_3\)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 transition temperature \( T_c\sim110 \) K and high critical current density \( (J_c) \) [1–3]. During the
powder in tube (PIT) process, deformation of Bi-2223/Ag composites is very important from the viewpoint of Bi-2223/Ag superconducting tape performance considering the density and the final microstructure of the superconducting cores are two of the dominating factors for the current capacity [4-7]. Core density influences the kinetics of 2223 phase creation and finally the quality of inter-grain connectivity: a higher core density results in a higher \( J_c \) [8,9]. The interfacial between the Ag sheath and the oxide core is very important for the current flow and texture formation, considering that the interface areas carry higher current than the core area. The wavy interface will severely interfere the texture formation of Bi-2223 grains along the metal sheath, and reduce the high current capacity areas [10-12].

During drawing, the Ag sheath experiences work hardening, therefore intermediate annealing is necessary in order to prevent breaking of the wire. Thus, it is quite necessary to optimize the intermediate annealing of drawing process in the Ag sheathed tapes. A significant number of studies related to the drawing process of the Bi-2223/Ag composites have been published previously. It has been demonstrated that softening of the Ag sheath by annealing will enhance the formation of sausages [13] and decrease the core density, The authors argue that this is because that increasing number of anneals or annealing temperature and time will enhance the difference of deformation resistance between Ag and the oxide core. Wang et al [14] deduce that the effect of annealing procedure on sausages is more significant than that of particle size of precursor powder.

In the present study, aiming at the enhancement of current capacity of Bi-2223 tapes, the influences of intermediate annealing times during drawing on the monofilament density, Ag/oxide core interface morphology and critical current properties of Ag sheathed Bi-2223 tapes were systematically discussed. Due to the formation of more smooth interfaces and high core density, an enhancement of \( J_c \) over 14% was obtained by decreasing the annealing times from three to one. Meanwhile, the one time annealing procedure was also applied to Ag-Au sheathed tapes and a higher critical current density was achieved.

2 Experimental

Bi-2223 precursor powders with nominal composition of Bi\(_{1.76}\)Pb\(_{0.34}\)Sr\(_{1.93}\)Ca\(_{2.02}\)Cu\(_{3.06}\)O\(_{x}\) were prepared through co-precipitation process [15, 16] with the initial phase assemblage of (Bi, Pb)-2212, Ca\(_2\)CuO\(_3\) and CuO. Mono filament wires were fabricated first by packing the precursor powders into Ag sheath. Then a series swaging and drawing process were performed with different intermediate annealing times to draw the wires from \( \phi 12 \) mm to hexagon 1.51 mm. 1# sample was annealed in long tube furnace at 400 °C for 0.5 h at the diameter of \( \phi 12, \phi 3.95, \phi 2.02 \) mm, and 2# sample was annealed only at the diameter of \( \phi 2.02 \) mm. 3# sample was AgAu sheathed (Bi, Pb)-2223 (inner and outer sheaths are both AgAu ), and was also annealed only at \( \phi 2.02 \) mm. The intermediate annealing profile of different samples is shown in Table 1. 37-filamentary Ag sheathed (Bi, Pb)-2223 tapes were fabricated by reassemble the monofilament wires into AgMgNi sheath [17]. And after a series of swaging, drawing and rolling process, three different final tapes with the cross section dimensions of ~0.29×4.4 mm were obtained. The as-rolled tapes with the length of 20 cm were then thermo-mechanically processed in 7.5% O\(_2\)/Ar atmosphere by three heat treatments at 822, 826, and 780°C, respectively. An intermediate rolling step was adopted to develop a dense and aligned Bi-2223 phase structure.

The morphology of wires were observed by optical microscope after polishing. The core density of the wires were calculated as
where \( m \) is the overall weight of a \( l \) long piece of wire, \( A_{\text{Ag}} \) and \( A_{\text{core}} \) are the cross section area of Ag and core component, respectively, and \( d_{\text{Ag}} \) and \( d_{\text{core}} \) are the density of Ag and core, respectively. Micro-Vickers hardness HV0.25 (100 g, 15 s) was measured on the cross-section of wires to monitor the core density. The critical currents \( (I_c) \) at 77 K, 0~0.6 T with the field parallel to the rolling plane of the tape, were measured using a standard four-probe DC method with the criterion of 1 \( \mu \)V/cm. Critical current density, \( J_c \) was calculated as \( J_c = \frac{I_c}{A} \), where \( A \) is the cross section area of superconducting core.

### Table 1. Intermediate annealing profile of different samples.

| Sample number | Sheaths                  | Annealing times | Annealing size (mm) |
|---------------|--------------------------|-----------------|---------------------|
| 1#            | Ag+A EgMgNi              | 3               | φ12, φ3.95, φ2.02   |
| 2#            | Ag+A egMgNi              | 1               | φ2.02               |
| 3#            | AgAu+A gAu              | 1               | φ2.02               |

### 3 Results and discussion

#### 3.1 Density and hardness changes during drawing

Density measurements of monofilament wire with different size (from φ3.95 mm to φ1.64 mm) of the samples are shown in figure 1, where \( D_0 \) refers to the starting size of monofilament wire (φ12mm), \( D \) refers to actual size. For 1#, 2# and 3# samples, the initial packing density is mostly the same, about 3.06g/cm\(^3\). It is clearly seen that the density of 1# sample is always the lowest among all the samples, especially at the beginning of drawing process. It reaches the maximum value of 4.93 g/cm\(^3\) at the diameter of ~φ2.11 mm. The densities of 2# and 3# sample are almost the same along the drawing process, which both reach the maximum value of ~5.06 g/cm\(^3\) simultaneously at the diameter of φ2.02 mm. However, the final density of 3# is obviously higher than that of 2# after the final annealing process at φ2.02 mm. The 1# wire is annealed for three times as marked in figure 1, the annealing process can obviously lead to the softening of the sheath. Therefore, the constrain stress applied on ceramics core is smaller after annealing and cause the decrease of core density. The maximum stress applied during drawing is limited by the strength of the Ag sheath. Thus the adoption of AgAu alloys could make it possible to apply larger drawing stress and therefore increase the final density without breaking the wire, so the density of 3# sample is highest at the final dimension.

There was a common fact that the density fluctuated for three samples, this appeared to be real, and not caused by uncertainty in the measurements. The reason was that the critical density was reached. If the powder-flow model was used, further deformation will not increase the density, but produced cracks due to the brittleness of the BiSrCaCuO materials [18]. If the density is evaluated from the change of volume this crack formation will result in an apparent decrease in density. These cracks can be healed by further drawing so the density increases again.

Micro-Vickers hardness values of monofilament wires with different sizes (from φ3.95 mm
to $\phi1.64$ mm) of different samples are shown in figure 2. Micro-Vickers hardness values are measured at the center of ceramic core. It is clearly seen that the hardness of 1# sample is the lowest, and reaches the maximum value of 80.6 also at the diameter of $\sim\phi2.11$ mm. The hardness values of 2# and 3# wires are almost the same before the annealing at $\phi2.02$ mm, and both reached the maximum values of 85.0 and 94.3 at the diameter of $\phi2.02$ mm. And after annealing the hardness values of 3# are all higher than those of 2#. The changing trend of hardness is consistent with that of core density. Figure 3 shows the Micro-Vickers hardness values of core as a function of core density. A linear relationship can be observed between the core density and hardness, which verifies the both results in figure 1 and figure 2.

3.2 Cross-section morphology of monofilament
Cross-section images of monofilament wires with different sizes are shown in figure 4. It reveals that the interfaces between the Ag sheath and the oxide core is rough for 1# sample, while the interfaces for 2# and 3# samples are much more smooth. It is because that the strength of the sheath material has an obvious influence on the Ag/oxide core interfaces. Considering that the yield strength of Ag is lower than that of ceramic powders, the deformation behaviors of metal sheath and ceramic core are different during the drawing process. Sample 1# has been annealed for three times, and the strength of Ag sheath will decrease after every annealing, but the strength of powder essentially constant. Thus the
deformation difference between sheath and ceramic powder is larger than that of 2# and 3# wires. Therefore, the deformation at Ag/core interface is more uniform in 2# and 3# sample and the formation of wavy interface is successfully avoided. For 3# sample, the sheath is AgAu alloy, the strength of which is higher than that of Ag, so the interface is smoother and the final core density is higher.

![Micrographs of cross-section of monofilament wire with different size](image)

**Figure 4.** Optical micrographs of cross-section of monofilament wire with different size

### 3.3 Critical current density

Figure 5 shows the $J_c$ values (77 K, 0 T) of Bi-2223 tapes of 1#, 2# and 3# samples after heat treatment. It can be noticed that the $J_c$ values increase from 17.9 kA/cm$^2$ of 1# sample to 20.5 kA/cm$^2$ of 2# sample with the decrease of intermediate annealing from three to one time. The 15% enhancement of $J_c$ suggests that the optimized intermediate annealing of drawing process for our Ag sheathed Bi-2223 wire is one time. Meanwhile, one time annealing procedure has also been adopted on Ag-Au sheathed tape. And a $J_c$ value of 16.3 kA/cm$^2$ is achieved, which is higher than the results obtained in our previous experiments (the phase evolution process of AgAu sheathed Bi-2223 tapes is different with that of Ag sheathed tapes attributed to the slower oxygen penetration rate of AgAu alloy, Nowadays, the obtained current capacity of AgAu sheathed tapes is still ~30% lower than that of Ag sheathed tapes).
Figure 5. $J_c$ values (77 K, 0 T) of 37-filament tapes of 1#, 2# and 3# samples

Fig 6 showed normalized $J_c/J_c(0)$ value in magnetic field applied parallel to the tape surface. It can be noticed that the $J_c/J_c(0)$ value of 2# sample is higher than that of 1# sample at low magnetic field. And they are mostly the same with the magnetic field increases up to 0.3 T. It implies that inter-grain connections of tapes are improved with the application of one time intermediate annealing, attributed to the increased density of ceramic core.

Figure 6. Normalized $J_c/J_c(0)$ value in magnetic field applied parallel to the tape surface

General speaking, there are two factors which mainly affect the critical current density of Bi-2223 tapes in our study, namely the superconducting core density and the Ag/superconducting core interface morphology. The density of the superconducting core should be sufficiently high. A higher density core directly correlated to more effective current carrying areas and a smaller crack density. Crack inside the superconducting core could limit $J_c$ or even block the current completely. Such a core has more effective current carrying areas and good connectivity, so it always results in a higher $J_c$. And low density area should be smaller to increase the effective current carrying area. Therefore, the high density core of 2# sample lead to the higher current capacity.

On the other hand, the interface morphology is another important factor which can influence the formation of textures along the interface and effective current carrying area. The interface is crucial for the textural alignment of Bi-2223 grains near interface. Meanwhile the textural alignment is better near Ag/superconducting core interface than in the center of the superconducting core. Therefore, a rough interface may have an undesired influence on the
alignment of Bi-2223 grains. Moreover wavy interface will reduce the actual cross-section area of the superconducting core and, therefore reduce the overall critical current. So the smooth interface in 2# sample with one time intermediate annealing is benefit to the high current capacity.

4. Conclusion

In this study, the influences of intermediate annealing times of drawing process on the core density, morphology and transport properties of Bi-2223 tapes were systematically investigated. Experimental results showed that with the decrease of annealing times from three to one, both the core density and the Vickers micro-hardness values of superconducting core increased consistently. Meanwhile, the Ag/oxide core interfaces became more smooth. Attributed to the higher superconducting core density and flat Ag/core interface, the maximum $J_c$ value of 20.5 kA/cm² and higher $J_{c}/J_{c}(0)$ value was obtained on the Bi-2223 tapes with one times intermediate annealing, which is ~15% higher than that of the wires with three times intermediate annealing. Moreover, the one time annealing procedure was also effective to Ag-Au sheathed tape, and a $J_c$ value of 16.3 kA/cm² has been achieved.

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