Evolution of Core Density of Ag-Clad Bi-2223 Tapes during Process

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Abstract—**The porosity and its effect on critical current density J_c of Ag-clad $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (Bi-2223) tapes throughout important steps in their thermomechanical treatment was investigated by using mass density measurement, microstructural observation, and superconducting property characterization. The relative mass density of the final filament for 19 filament tape was less than 75%, even though the J_c is ~50 kA/cm^2 (77K, 0T). The mass density in monofilaments reached 90%, because retrograde densification during the first heat treatment (HT1) was less or even absent. Well textured Bi-2223 grain growth could result in a significant densification during the first HT in the monofilament composite. Our results hint at considerable variability in this important property of Bi-2223 tape.**

Index Terms—**$(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ tape, porosity, mass density, critical current and microstructure**

I. Introduction

The thermomechanical processing of Ag-sheathed $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (Bi-2223) tapes is a complex, multi-step process which typically involves 2 to 3 heat treatments with intermediate deformation steps[1]-[3]. An underlying issue is the tendency of composites to swell during heat treatment. It is generally believed that this retrograde densification occurs during the formation of the Bi-2223 phase[4],[5]. An important role of the intermediate deformation(s) is thus to re-densify the core prior to the second or third heat treatment. However, the causes for retrograde densification are not clear, nor is its magnitude. Yamada et al. showed that a relative mass density increase from 72% to 78% correlated to a J_c increase from 10 to 66 kA/cm^2 (77K, 0T)[4]. Micro-hardness can also be used as an indicator of mass density and porosity. A very strong correlation between indentation hardness of Bi-2223 tapes and their J_c (77K, 0T) value was established by Parrell et al. [6],[7]. The J_c was seen to increase much more strongly than linearly as hardness increased. Subsequent tests of this correlation between mass density and J_c have been rare, particularly for multifilament tapes, partly because small filament size (~10μm thick and ~200 μm wide) makes density and hardness measurements uncertain. The purpose of the present work was to study the mass density variation through-process and correlate it with the properties of the state-of-the-art R&D Bi-2223 tapes.

Manuscript received September 18, 2000. This work was supported by the Department of Energy - Energy Efficiency and Renewable Energy and also benefited from partial support from the National Science Foundation – MRSEC.

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II. Experimental

The experimental 19 filament Bi-2223 tapes of the study were prepared at American Superconductor Corporation [8] using a thermomechanical treatment based on two heat treatments and one intermediate rolling. Samples listed in Table 1 were taken at the end of each important processing stage, that is before heat treatment (BHT), after HT1, after the intermediate rolling step (IR), and after HT2. The samples have dimensions 1.9 by 0.1 mm.

Monocore Bi-2223 composites were made at UW using standard powder in tube process. Bi-2223 precursor powder was packed into a Ag tube which was then closed. The packed Bi-2223 billets were annealed in N_2 or 7.5% O_2 for a time from 2 to 12 hours. Thus, four monocore composites were prepared, as listed in Table 2. 2.0 mm diameter wires were rolled to 150 μm thick tape using 38 mm diameter work rolls. The first heat treatments was done at 825°C in a flowing 7.5% O_2/balance N_2 atmosphere. After this first HT, the tape thickness was then reduced by 15-20% in one pass using 152 mm rolls. Tapes were then heat treated for an additional 24 hours at 827°C, 48 hours at 822°C and 24 hours at 805°C. Monocore samples listed in Table 2 were taken at the end of each processing stage, that is before heat treatment (BHT), after HT1 (HT1), after the intermediate rolling step (IR), and after the second heat treatment (HT2).

The filament areas were measured for each sample by

TABLE 1
CRITICAL CURRENT DENSITY J_c (77K), MASS DENSITY (ρ, g/cm^3), AND RELATIVE DENSITY (ρ) FOR 19 FILAMENT TAPES AT DIFFERENT PROCESS STAGES

Processing stage	J_c (self field) (kA/cm^2)	J_c (0.1T) (kA/cm^2)	ρ (g/cm^3)	Relative density[a]
BHT	—	—	5.6	89%
HT1	14.7	2.1	4.4	70%
IR	2.8	—	5.6	89%
HT2	49.4	13.0	4.6	73%

[a]Mass density of Bi-2223 phase = 6.3 g/cm^3 [9].

TABLE 2
MONOFILAMENT COMPOSITE ANNEALING CONDITION, CRITICAL CURRENT I_c (77K, self field) AND CRITICAL CURRENT DENSITY J_c (77K, self field)

Composite	Pre-deformation annealing	I_c(A) after HT1	I_c(A) after HT2	J_c (kA/cm^2) after HT2
UWB-A	785°C/2 hours in N_2	3.0	32.5	20.6
UWB-B	785°C/6 hours in N_2	4.2	42.3	28.8
UWB-C	785°C/12 hours in N_2	7.6	31.7	24.4
UWB-D	790°C/2 hours in 7.5% O_2	1.0	16.5	10.9

digital image analysis of the Ag and Bi-2223 cores in three cross-sections. The filament mass density of the 19-filament tape was calculated on the assumption that the filament and silver are longitudinally uniform and that the silver sheath is 100% dense throughout the process and only the Bi-2223 core density changes. The uncertainty of mass density on ~10 μm thick filaments is believed to be ~ ±5%. The mass density of monofilament composites was measured by image analysis of the core area and direct weighing of the core after etching away the silver with a 2.5:1 mixture of NH_4OH and H_2O_2 (30%).

The critical current density (77 K, 0 T, 1 μV/cm) of these tapes was measured using standard four terminal techniques. Polished transverse and longitudinal sections of the tapes were studied using a JSM-6100 Scanning Electron Microscope (SEM) operated in backscatter mode.

III. RESULTS AND DISCUSSION

A. Critical current and mass density variation through process of 19 filament tape

The critical current density and filament mass density of 19 filament tape are given in Table 1. The J_c at 0T and at 0.1 T changed strongly from HT1 to HT2, rising to 14.7 kA/cm^2 (2.1 kA/cm^2 at 0.1T) after the first heat treatment (HT1), falling to 2.8 kA/cm^2 after the intermediate rolling (IR), then rising to 49.4 kA/cm^2 (13.0 kA/cm^2 at 0.1T) after HT2.

The filament mass densities fell from an initial value of 5.6 g/cm^3 before HT, to 4.4 g/cm^3 after HT1, rising to 5.6 g/cm^3 again after intermediate rolling (when J_c was significantly reduced), then falling again to 4.6 g/cm^3 after the final heat treatment. It is clear that substantial dedensification occurs in each HT (22% loss after HT1, 18% after HT2) and that intermediate rolling has a very important role to play in returning the mass density to a high value prior to the second HT. It is also striking that the final density is only 73% compared to that of a fully dense Bi-2223 filament. Significant porosity, cracking and undesirable second phase all contribute to this low density, which cannot be beneficial either to the electrical or to the mechanical integrity of the filaments.

B. Microstructure of monocore composites

Fig. 1 shows the X-ray diffraction patterns of as-rolled monocore composites UWB-A to UWB-D, listed in Table 2. These composites were made from the same precursor with the same mechanical deformation. The only difference between them is the pre-deformation annealing conditions. The pre-deformation annealing was introduced in order to change the phase assemblage in the precursor, especially for reducing the amount of $(Ca,Sr)_2PbO_4$. This could lead to the fast formation of the Bi-2223 phase [10]. As shown in Fig.1, the relative intensity of the (011) peak (at 2θ=17.6°) of $(Ca,Sr)_2PbO_4$ was reduced from 0.53 for composite UWB-A to 0.21 for UWB-B, 0.13 for UWB-C and 0.29 for UWB-D.

It is believed that Pb (whether in Bi-2212 or in $(Ca,Sr)_2PbO_4$) plays a key role in the formation of Bi-2223[10]-[12]. Incorporating Pb into the Bi-2212 can accelerate the nucleation of the Bi-2223[10],[11], but the presence of $(Ca,Sr)_2PbO_4$ can promote the formation of the liquid, which is important to the growth of the Bi-2223. Fig. 2 shows the backscattered electron microscope images of monocore composites UWB-A to UWB-D sintered for 12 hours at 825°C in 7.5%O_2 balance N_2 atmosphere. The formation of the Bi-2223 phase at the initial stage is significantly different for the four composites. There exist only a few Bi-2223 grains near the silver interface in UWB-A and UWB-B after the 12 hour sintering. Much more Bi-2223 forms in UWB-C, the microstructure of which is the most

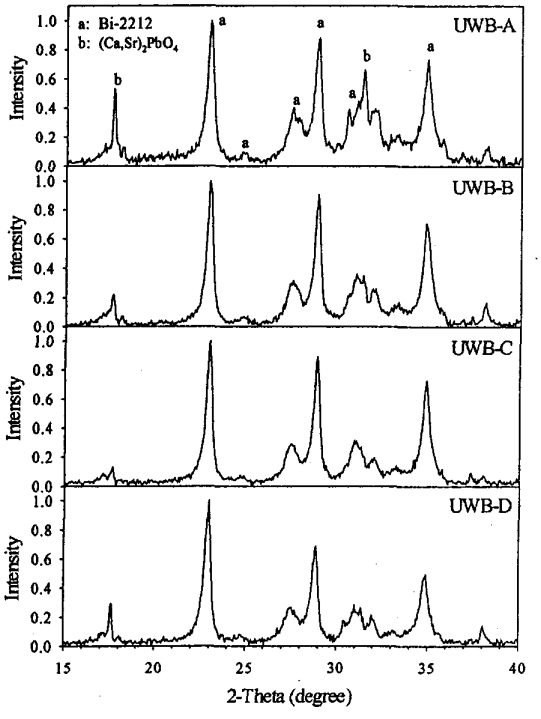

Fig. 1. X-ray diffraction patterns of as-rolled monocore composites. The diffraction intensity was normalized by the intensity of $(008)_{2212}$ peak (at 2θ = 23°). The peak at 2θ = 17.6° is a line corresponding to $(Ca,Sr)_2PbO_4$.

TABLE 3
MASS DENSITY (ρ, g/cm^3) AND RELATIVE DENSITY FOR MONOCORE COMPOSITES AT DIFFERENT PROCESSING STAGES

Composite	BHT	HT1	IR	HT2
UWB-A	4.71	5.17	5.68	5.48
	(75%)	(82%)	(90%)	(87%)
UWB-B	4.82	5.30	5.86	5.62
	(77%)	(84%)	(93%)	(89%)
UWB-C	5.08	4.78	5.76	5.67
	(816%)	(76%)	(91%)	(90%)
UWB-D	4.96	4.28	—	5.32
	(79%)	(70%)		(84%)

Mass density of Bi-2223 phase = 6.3 g/cm^3 [9].

homogeneous. The alignment of Bi-2223 grains in UWB-D is worst. This indicates that the nucleation, growth and alignment of Bi-2223 are related to the phase assemblage of the precursor and its deformation processing.

Fig. 3. shows the backscattered electron microscope images of monocore composites UWB-A to UWB-D after the first heat treatment (sintering for 36 hours at 825°C in 7.5%O_2 balance N_2 atmosphere). The formation of Bi-2223 in UWB-A and UWB-B were slower than UWB-C and UWB-D, but well textured large Bi-2223 grains formed in UWB-A and UWB-B.

C. Critical current and mass density variation through process of monofilament tapes

The critical current I_c and critical current density J_c are given in Table 2 for the four monocore composites. Composite UWB-C shows the highest I_c after the first HT, which resulted from the faster formation of Bi-2223 phase, as shown in Fig. 2. The lowest I_c value after HT1 for UWB-D is believed to be due to the large misalignment of Bi-2223 grains. I_c value of 42.3 A, corresponding to J_c of 28.8 kA/cm^2, achieved in fully processed UWB-B.

Table 3 gives the mass density and relative mass density for the monocore composites at the end of each processing stage. It is generally believed that retrograde densification always occurs during the formation of Bi-2223[4],[5]. It is surprisingly seen that UWB-A and UWB-B both densified during HT1, while there was a retrograde densification only in UWB-C and UWB-D. This means that the occurrence of retrograde densification greatly depends on processing. The

TABLE 4
MONOCORE COMPOSITE FILLING FACTOR (F) AT DIFFERENT PROCESSING STAGES

Composite	BHT	HT1	IR	HT2
UWB-A	0.399	0.351	0.343	0.358
UWB-B	0.375	0.344	0.324	0.325
UWB-C	0.364	0.368	0.313	0.310
UWB-D	0.367	0.386	—	0.333

Filling factor F is a ratio of core to whole composite cross section.

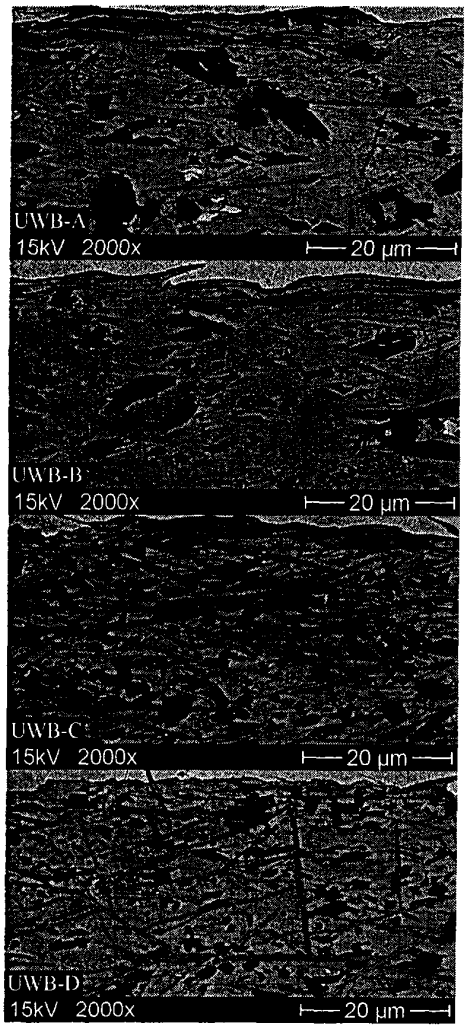

Fig. 2. Backscattered electron microscope images taken on transverse cross sections of monocore composites UWB-A to UWB-D sintered for 12 hours at 825°C in 7.5% O_2 balance N_2 atmosphere. The top of each image is at the interface of silver and core, and the bottom is at the central region of the core. The light gray regions, dark gray needle like grains and black particles are Bi-2212, Bi-2223 and alkaline-earth cuprates, respectively.

densification during HT1 for UWB-A and UWB-B is confirmed by the decrease of BSCCO filling factor because of the decrease of the core area during HT1. The increase of density given in Table 3 corresponds to the decrease of filling factor in Table 4. We believe that the formation of well textured Bi-2223 grains in composites UWB-A and UWB-B leads to densification, while misaligned growth of the Bi-2223 in composite UWB-D is the cause for the significant dedensification during the HT1. The density of composite UWB-B after HT1 was 5.3 g/cm^3 (84% dense), which is very close to that of a fully processed monofilament tape with J_c of 35 kA/cm^2 (77K, 0T) [13]. This suggests that it might be possible to make high J_c tapes with only one heat treatment when there is no dedensification during the heat treatment.

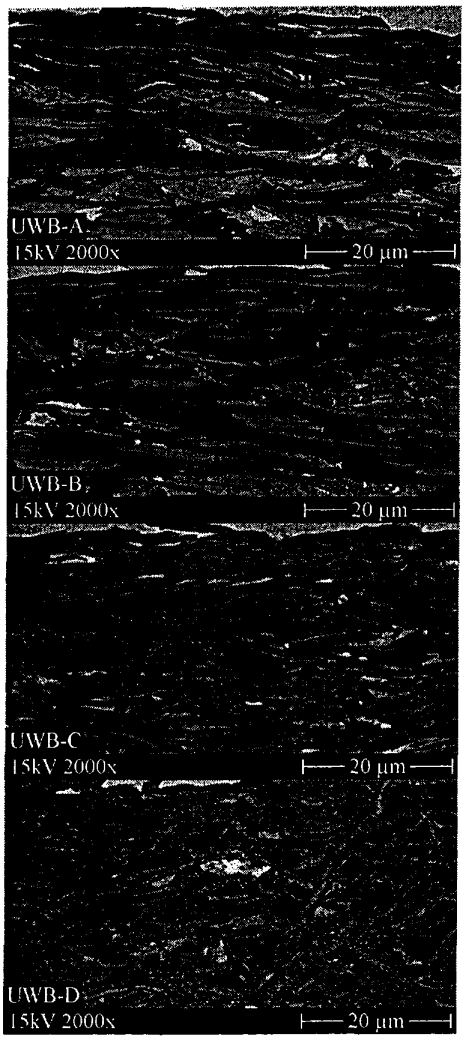

Fig. 3. Backscattered electron microscope images taken on transverse cross sections of monocore composites UWB-A to UWB-D after the first heat treatment (sintering for 36 hours at 825°C in 7.5% O_2 balance N_2 atmosphere). The top of each image is at the interface of silver and core, and the bottom is at the central region of the core. The light gray, dark gray regions, and black particles are Bi-2212, Bi-2223 and alkaline-earth cuprates, respectively.

Table 3 also shows that intermediate rolling really densified the monofilaments and that the density values after the HT2 are very close to that after the intermediate rolling. This means that the dedensification for monofilament tape is not significant during HT2. The monofilament is 85-90% dense after the HT2, compared to that of a fully dense Bi-2223 filament.

IV. Summary

We have investigated the density variation through process for both multifilament and monofilament Bi-2223 tapes. We found much larger changes in the 19-filament tape. The relative mass density of the final filament for 19 filament tape was less than 75%, even though the J_c attains ~50 kA/cm^2 (77K, 0T), while monofilaments with J_c of 11-29 kA/cm2 had densities of 84-90%. Thus there is no simple general correlation of density and J_c. The retrograde densification during the first heat treatment was found to depend greatly on powder pretreatment and that some treatments produced a rising density during the first heat treatment. This could point a way for producing the Bi-2223 in only one heat treatment if high density can be achieved before the heat treatment and dedensification avoided during the heat treatment. Our result also shows that dedensification during the second heat treatment is not remarkable for monofilament tape.

Acknowledgment

We are grateful to A. A. Polyanskii (UW), Vic Maroni (ANL), Terry Holesinger and Jeff Willis (LANL), and Dominic Lee and Don Kroger (ORNL) for illuminating discussions. We thank W. L. Starch for experimental assistance.

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