The Effect of Oxygen Partial Pressure during Heat Treatment on the Microstructure of Dip-coated Bi-2212/Ag and Ag Alloy Tapes

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Abstract---**The evolution of the microstructure during heat treatment was investigated for dip-coated $Bi_2Sr_2CaCu_2O_y$(Bi-2212)/Ag and Ag alloy tapes as a function of temperature and oxygen partial pressure(P_{O2}=0.01, 0.21 and 1 atm) using quenched and fully-processed tapes. The microstructures were essentially the same for Bi-2212 on pure Ag and on the Ag alloy. Although the melting temperature of Bi-2212 increased with increasing P_{O2}, the solidification temperature(T_{sol}) of Bi-2212 for P_{O2}=0.21 atm was higher than that for P_{O2}=1 atm. The volume fraction and grain alignment of Bi-2212 processed in P_{O2}=0.01 atm was smaller than in tapes processed in 0.21 and 1 atm, which were quite similar. HR-TEM studies on grain boundaries and AC susceptibility measurements suggest that the higher critical current density(J_c) for tapes processed in P_{O2}=1 atm than that for 0.21 atm is due to improved coupling of the grains.**

I. INTRODUCTION

Bi-2212/Ag composite tape is one of the promising materials for application in wires and coils at low temperature due to its high critical current density (J_c) [1],[2]. It was reported that the J_c was influenced by oxygen partial pressure (P_{O2}) during processing [3]-[5]. We reported that the J_c values of Bi-2212/Ag tapes were 0.5, 1.2 and 2×10^5 A/cm^2 (4.2 K,10 T) when processed in P_{O2}=0.01, 0.21 and 1 atm, respectively [3]. From practical applications, a Ag alloy with higher strength than pure Ag is preferred to withstand the large Lorenz force in high magnetic fields [6],[7]. The yield strength of the Ag alloy tapes used in this study was twice of that of pure Ag [8]. In this study, we investigated the evolution of the microstructure during heat treatment for dip-coated Bi-2212 on pure Ag and Ag alloy tapes as a function of temperature and P_{O2} using quenched and fully-processed tapes. The relationship between the microstructure and J_c of the Bi-2212/Ag alloy tapes processed in various P_{O2} is discussed in comparison with the results of Bi-2212/Ag tapes by doctor-blade method [3].

II. EXPERIMENTAL

Bi-2212, of overall composition $Bi_2Sr_2Ca_{0.96}Cu_2O_y$ was dip-coated on Ag and Ag alloy tape. The alloy composition was Ag-0.067at%Mg-0.019at%Zr. The tapes were heated up to the maximum processing temperature, T_{max}, which varied with the processing P_{O2}. The T_{max} that gave the highest J_c was 840, 880 and 885 °C for P_{O2}=0.01, 0.21 and 1 atm, respectively [3]. The tapes were held at T_{max} for 5 minutes, then cooled down at 10 K/hr for 5 hrs, and finally furnace-cooled to room temperature. For the microstructural analysis, tapes were quenched into an oil bath every 5 °C during cooling from T_{max}. The surface and polished cross sections of the tapes were examined with a scanning electron microscope (SEM) using backscattering electron image. The phases were identified using energy dispersive X-ray spectroscopy (EDX) on the SEM. X-ray diffraction (XRD) was performed on the tape surface and rocking curves were measured to investigate grain alignment. High-resolution electron microscopy (HR-TEM) images of Bi-2212 grain boundaries were recorded using a JEOL JEM-4000EX. HR-TEM specimens were prepared by grinding, dimpling and finally ion milling with a liquid nitrogen cooled stage. AC susceptibility measurements were performed in magnetic fields ranging from 0.02 to 2 Oe.

III. RESULTS AND DISCUSSION

Fig. 1 shows the typical microstructure of tapes with Ag alloy substrates quenched from T_{max} in the different P_{O2}s. At T_{max}, the melt contains liquid, and Bi-free and Cu-free nonsuperconducting phases. The identity of the nonsuperconducting phases varied with P_{O2}. Table I summarizes the phases found in tapes on Ag and the Ag alloy at different temperatures while processing in the different P_{O2}s. There is no difference in the phase assemblage or the composition of the nonsuperconducting crystalline phases on pure Ag and the Ag alloy at each temperature for the different P_{O2}s. Although the melting temperature of Bi-2212 increased with increasing P_{O2}, the solidification temperature (T_{sol}) of Bi-2212 for P_{O2}=0.21 atm was higher than that for P_{O2}=1 atm on both pure Ag and the Ag alloy. Similar results were reported for Ag-sheathed Bi-2212 conductors [4].

Fig. 2 shows the typical microstructure of the tapes with Ag alloy substrates fully processed in the different P_{O2}s. Comparing Figs. 1 and 2, we see that most of the liquid and nonsuperconducting crystalline phases were consumed as the Bi-2212 formed during cooling. The fully processed tapes were

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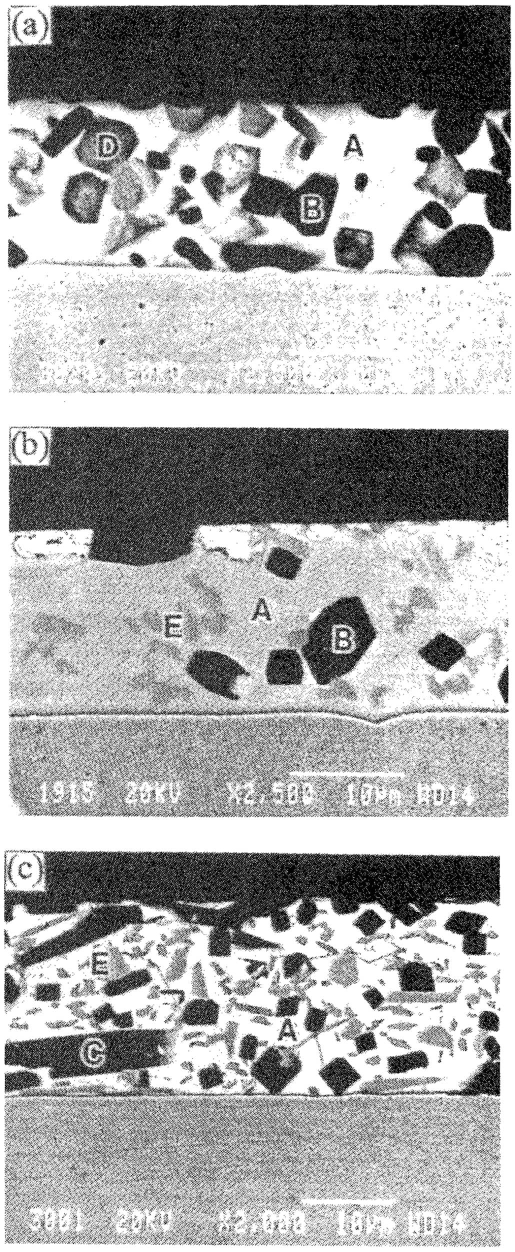

Fig. 1. Backscattered electron images of polished cross sections of Bi-2212/Ag alloy tapes quenched from T_{max}, (a) 840 °C in P_{O2}=0.01 atm, (b) 880 °C in P_{O2}=0.21 atm, and (c) 885 °C in P_{O2}=1 atm. A=liquid, B=(Sr,Ca)CuO$_y$, C=(Sr,Ca)$_{14}$Cu$_{24}$O$_y$, D=Bi$_2$(Sr,Ca)$_3$O$_y$, E=Bi$_2$(Sr,Ca)$_4$O$_y$.

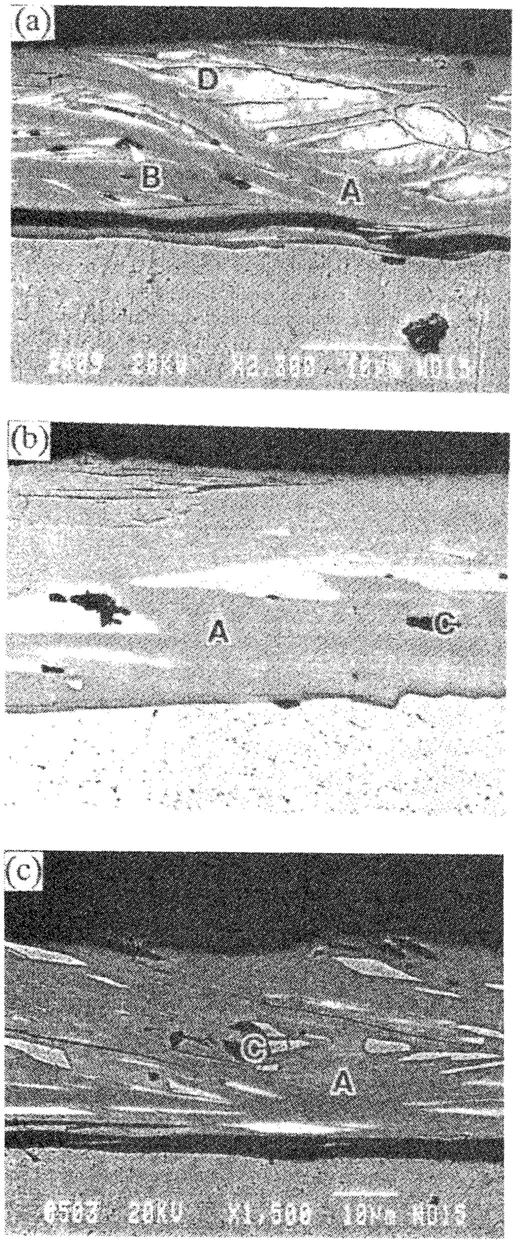

Fig. 2. Backscattered electron images of polished cross sections of Bi-2212/Ag alloy tapes fully processed in P_{O2}= (a) 0.01, (b) 0.21, and (c) 1 atm. A=Bi-2212, B=(Sr,Ca)CuO$_y$, C=(Sr,Ca)$_{14}$Cu$_{24}$O$_y$, D=Bi$_2$(Sr,Ca)$_3$O$_y$.

free of remnant grains of the Bi-free phase except for the tape processed in P_{O2}=0.01 atm where both Bi-free and Cu-free phases were observed.

The volume fraction of nonsuperconducting crystalline phases and pores was greatest in the melt for tape processed in P_{O2}=0.01 atm (Fig. 1) and was smaller in tapes processed in P_{O2}=0.21 and 1 atm. The tape processed in P_{O2}=1 atm had a rougher surface than tape processed in P_{O2}=0.21 atm (Fig. 2). X-ray rocking curves of $00\underline{10}$ reflection in Fig. 3 showed that the full width at half maximum (FWHM) was θ=10.0, 7.5 and 9.5 degree for tapes fully processed in P_{O2}=0.01, 0.21 and 1 atm. Although the different samples processed in the same P_{O2} gave different FWHM values, it was reproducible that the tape processed in P_{O2}=0.21 atm had better Bi-2212 alignment than the other atmospheres. J_c for P_{O2}=0.01, 0.21 and 1 atm are 0.5, 1.2 and 2×10^5 A/cm^2, respectively, at 4.2 K, 10 T [3]. The

TABLE I

Phase Assemblages Observed in Quenched Bi-2212/Ag Alloy Tapes Processed under Various P_{O2}. Samples Were Quenched Every 5 °C during Cooling from T_{max}. T_{max} Was 840, 880 and 885 °C for P_{O2}=0.01, 0.21 and 1 atm, Respectively. 14:24AEC, 1:1AEC, 2:3CF and 2:4CF Indicate $(Sr,Ca)_{14}Cu_{24}O_y$, $(Sr,Ca)CuO_y$, $Bi_2(Sr,Ca)_3O_y$ and $Bi_2(Sr,Ca)_4O_y$, Respectively.

T (°C)	P_{O2}=0.01 atm	P_{O2}=0.21 atm	P_{O2}=1 atm
885			liquid, 14:24AEC, 2:4CF
880-870		liquid, 1:1AEC, 2:4CF	liquid, 14:24AEC, 2:4CF
865-860		Bi-2212, 1:1AEC	liquid, 14:24AEC, 2:4CF
855-845		Bi-2212, 1:1AEC	Bi-2212, 14:24AEC
840-835	liquid, 1:1AEC, 2:3CF	Bi-2212, 1:1AEC	Bi-2212, 14:24AEC
830	Bi-2212, 1:1AEC, 2:3CF	Bi-2212, 1:1AEC	Bi-2212, 14:24AEC

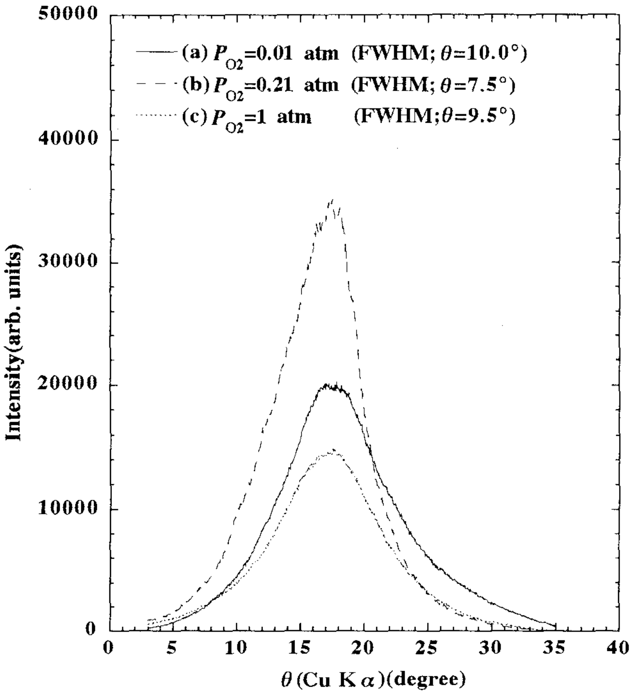

Fig. 3. X-ray rocking curves of 00<u>10</u> reflection of the Bi-2212/Ag alloy tape fully processed in P_{O2}= (a) 0.01, (b) 0.21, and (c) 1 atm. The full width at half maximum (FWHM) are θ=10.0, 7.5 and 9.5 for P_{O2}=0.01, 0.21 and 1 atm, respectively.

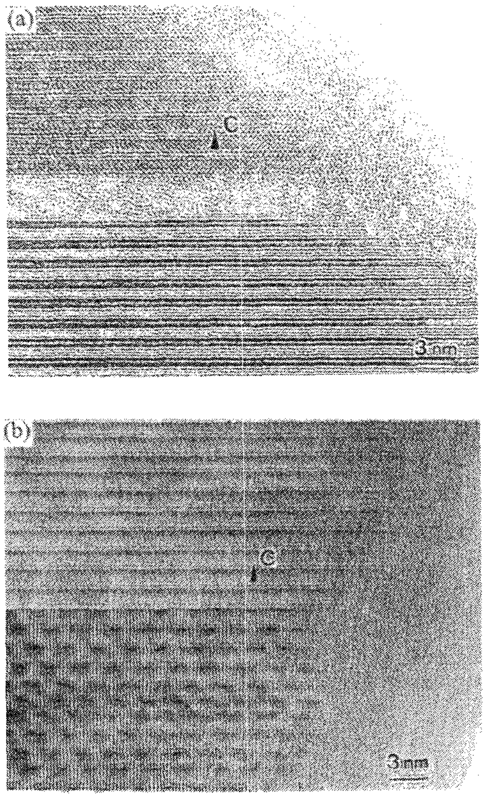

Fig. 4. HR-TEM images of two types of (001) twist grain boundaries observed in fully processed B-2212/Ag alloy tapes. (a) Twist boundary with an amorphous layer at the grain boundary. (b) Twist boundary without an amorphous layer at the grain boundary.

micrographs of the fully processed tape (Fig. 2) suggest that the lowest J_c in P_{O2}=0.01 atm is due to the smallest volume fraction of Bi-2212 in the fully processed tape. However, it is not apparent from the microstructures in Fig. 2 why J_c is higher in tape processed in P_{O2}=1 atm than in 0.21 atm.

There are several types of grain boundaries in the fully processed Bi-2212 tapes [9],[10]. The most frequently observed (001) twist boundaries were within a colony, while the rarely observed other boundaries like tilt boundaries were at the colony interface as in Ag-sheathed Bi-2212 conductors [10]. Fig. 4 shows HR-TEM images of two typical (001) twist boundaries in fully processed Bi-2212 on the Ag alloy. The incident electron beam is normal to c-axis. Fig. 4 (a) shows an amorphous region at the boundary that is a few nanometers thick. Fig. 4 (b) shows a clean boundary with no amorphous material at the boundary. Twist boundaries with amorphous

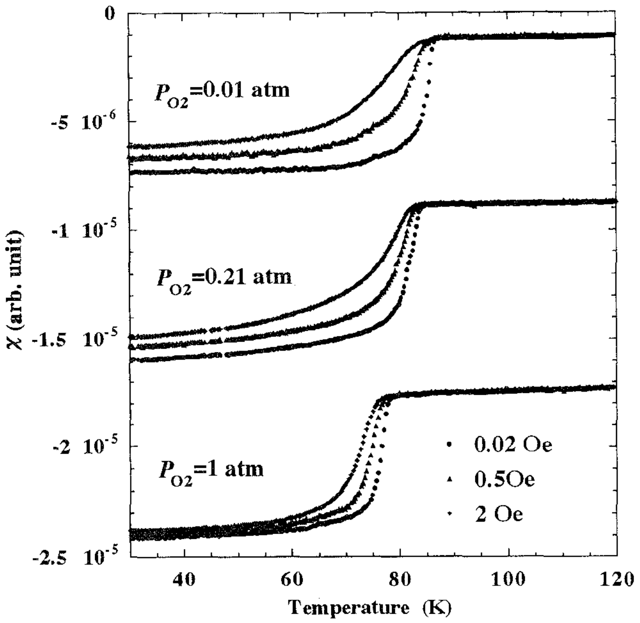

Fig. 5. Temperature-dependence of the real part of AC susceptibility curves of Bi-2212/Ag alloy tapes fully processed in P_{O2}=(a) 0.01, (b) 0.21 and (c)1 atm. The measurements were performed in fields of 0.02 to 2 Oe.

layers were frequently observed in tape fully processed in P_{O2}=0.01 atm. In tape fully processed in P_{O2}=1 atm, most of the twist boundaries did not contain an amorphous layer at the boundary. The population of twist boundaries with the amorphous layer was much lower for tape processed in P_{O2}=1 atm compared to those in lower P_{O2}, which was reproducible for a few different specimens prepared from the tapes processed in the same P_{O2}. These results were independent of the type of substrate.

The real part of AC susceptibility curves for Bi-2212/Ag alloy tapes showed less field-dependence for the tape fully processed in P_{O2}=1 atm compared to 0.01 atm, as shown in Fig. 5. Similar results were obtained for Bi-2212/pure Ag tapes [3]. This indicates the existence of weak grain coupling in tape processed in P_{O2}=0.01 atm compared to 1 atm. This is in agreement with the "brick wall" model [11], where the amorphous layer, which is assumed to be a normal region, would reduce the supercurrent that could flow in the *c* direction due to small coherence length of Bi-2212, thus reducing the grain connectivity in the *c* direction. However, we cannot exclude the "railway switch" model [12], since the HREM observations on small-angle tilt grain boundaries was not enough in this experiment.

The microstructure and AC susceptibility results suggest that the higher J_c of the tape fully processed in P_{O2}=1 atm compared to P_{O2}=0.21 atm is due to improved coupling of Bi-2212 grains in the P_{O2}=1 atm tapes.

IV. CONCLUSION

The microstructure and phase assemblages of Bi-2212/Ag and Ag alloy tapes depended on both P_{O2} and heat treatment temperature, but is essentially insensitive to the substrate. The volume fraction of Bi-2212 was larger in tapes fully processed in P_{O2}=0.21 and 1 atm than in P_{O2}=0.01 atm, but the volume fraction of Bi-2212 was essentially identical in tapes processed in P_{O2}=0.21 and 1 atm. The tape fully processed in P_{O2}=0.21 atm showed the best grain alignment. Microstructural studies and AC susceptibility measurements suggest that the high J_c observed for the tape processed in P_{O2}=1 atm is due to improved coupling between the Bi-2212.

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