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JOURNAL OF RARE EARTHS
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JOURNAL OF RARE EARTHS, Vol. 27, No. 3, Jun. 2009, p. 486

Effect of humidity on microstructure and properties of YBCO film prepared by TFA-MOD method

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Received 16 December 2008; revised 14 February 2009

Abstract: Epitaxial YBCO superconducting films were deposited on the single crystal $LaAlO_3$ (001) substrate by metal organic deposition method. All YBCO films were fired at 820 °C in humidity range of 2.6%–19.7% atmosphere. Microstructure of YBCO thin films was analyzed by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). Superconducting properties of YBCO films were measured by four-probe method. XRD results showed that the second phase (such as BaF_2) and *a*-axis-oriented grains existed in the films prepared at 2.6% humidity condition; *a*-axis-oriented grains increased in the film prepared at higher than 4.2% humidity condition; almost pure *c*-axias-oriented grains existed in the films fired at 4.2% humidity condition. Morphologies of the YBCO films showed that all films had a smooth and crack-free surface. YBCO film prepared at 4.2% humidity condition showed J_c value of 3.3 MA/cm^2 at 77 K in self-field.

Keywords: YBCO; TFA-MOD; coated conductor; superconductivity; rare earths

$YBa_2Cu_3O_{7-x}$ (YBCO) coated conductor has more advantages in mechanical strength, critical current density (J_c) under magnetic fields and losses in AC applications than those of $Bi_2Sr_2Ca_2Cu_3O_y$ (Bi2223). So YBCO coated films have been considered to be candidate materials for second-generation superconducting tapes. YBCO film can be prepared using various methods such as magnetron sputtering, vacuum evaporation, chemical vapor deposition (CVD), liquid phase epitaxy (LPE), pulsed laser deposition (PLD) and metal organic deposition (MOD). Among these methods, MOD process using trifluoroacetic acid (TFA) has several advantages, including precise controllability of metal content, wide range of coating materials that can be used, and low cost of the process because it does not require vacuum equipment. So, TFA-MOD method is considered to be one of the most promising methods[1–5]. The critical current of YBCO films depends on the formability of YBCO phase, existence of second phases, texture, grain connectivity, and film thickness, etc. Since fluoride could react with water vapor in the firing process, humidity (the partial pressure of water vapor in firing process) was indispensable to form strongly oriented YBCO grains in the firing process. Seok Hern Jang et al.[6] studied YBCO films fired at 775 °C in the 0%–20% humidified Ar gas mixed with 1000 ppm oxygen. They found that the optimum humidity in the firing process at 775 °C was 12.1%–20%. T. Araki et al.[7] also studied YBCO films fired at 800 °C in the 0%–20% humidified Ar gas mixed with 1000 ppm oxygen, they found films fired at 4.2% humidified atmosphere was the best and films fired with >4.2% humidity condition did not show obvious degradation compared with films fired with 4.2% humidified atmosphere. However, effects of the humidity during heat treatment on microstructures and the critical properties have not been systematically studied in humidified N_2 gas mixed with O_2.

In our study, to reduce cost the common industrial N_2 gas mixed with 5vol.% O_2 was used as inlet gas and non-vacuum equipment for industrial preparation of YBCO. The firing temperature was 820 °C in our previous work[8]. The films were fired in atmospheres containing various levels of humidity to evaluate variation in microstructures and superconducting properties with humidity.

1 Experimental

The TFA precursor solution for fabricating the YBCO films was prepared by dissolving Y-, Ba-, and Cu-acetates in TFA with molar ratios of Y:Ba:Cu=1:2:3 and refluxing the mixture at 70 °C for 4 h. The solution was then dried in an oven to evaporate TFA and residual acetic acids, resulting in

Foundation item: Project supported by the National 863 Program of Ministry of Science and Technology of China (2007AA03Z216)

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DOI: 10.1016/S1002-0721(08)60274-4

a blue-colored solid residue, which dissolved readily in methanol with a total metal ions concentration of 1.5 mol/L.

The solution was deposited on $LaAlO_3$ substrates (10 mm× 10 mm) by spin coating method at 3000 r/min for 1 min. The coated films were subjected to two stages of heat treatments, which include lower temperature calcination and high temperature crystallization. The calcining process was performed at 400 °C for 8 h in a flowing 4.2% humidified oxygen atmosphere. The calcined films were fired at 820 °C for 1 h 30 min in 2.6%–19.7% humidified N_2 gas mixed with 5vol.% O_2 (hereafter, referred to as 2.6%, 4.2%, 5.6%, 7.3% and 19.7% humidity). The fired films were then heat treated at 450 °C for 1 h in dry oxygen (oxygen heat treatment) to optimize the oxygen content in YBCO. In this experiment, the gases used were industrial N_2 and O_2, and their purity was 98% and 99%, respectively. For convenience, hereafter samples fired at 2.6%, 4.2%, 5.6%, 7.3% and 19.7% humidity were referred as S1, S2, S3, S4, and S5, respectively.

The YBCO films were studied by X-ray diffraction (XRD) and scanning electron microscope (SEM) to evaluate phase identification and surface microstructure. The critical current (J_c) measurement and T_c were carried out by four-probe method to evaluate superconducting properties.

2 Results and discussion

Fig.1 shows XRD patterns of S1, S2, S3, S4, and S5. Fig.1(b) is partially magnified image of Fig.1(a). The figures show that the YBCO (00l) plane is parallel to the surface in all films which indicate well-developed *c*-axis orientation. Second phases such as BaF_2, $Y_2Cu_2O_5$ and CuO appear in S1 and almost pure YBCO phase is observed in S2, S3, S4, and S5. However, YBCO (200) exist in the films except sample S2. The existence of YBCO (200) means that there are a-axial oriented grains in the films. Smith et al.[9] considered that the overall reaction for the formation of YBCO phase in firing process can be expressed as follows:

$$0.5Y_2Cu_2O_5+2BaF_2+2CuO+2H_2O\rightarrow YBa_2Cu_3O_{7-x}+4Hf(g) \quad (1)$$

According to the law of mass action, the higher humidity (i.e., higher partial pressure of H_2O) enhances the driving force of the reaction and promotes the nucleation of YBCO. Therefore, low humidity might results in incompleted formation of YBCO during the firing process causing BaF_2, $Y_2Cu_2O_5$ and CuO remained in the films in sample S1. The higher humidity may cause fast reaction and confused growth of YBCO. For samples S1, S3, S4 and S5, there are YBCO (200) in the films. For sample S2, the YBCO (00l) peak is stronger and no (200) peak and second phase exist, indicating that its crystallization integrality is the best among all the as-prepared samples.

Analysis of (103) and (005) pole figures was conducted to evaluate the texture of the films, as shown in Fig.2. Fig.2(a) shows the pole-figure of sample S1. The figure shows that the major texture is biaxial, and other minor texture components are also present. The presence of these minor components may result from the formation of BaF_2 and other phases. The remaining phase such as BaF_2 may have an adverse effect on the texturing of YBCO films. From the pole figures, we discovered that a sharp and strong biaxial texture was formed without minor texture components and their poles were symmetric for samples S2, S3, and S4. It indicates that pure YBCO without second phases resulted in stronger texture. On the other hand, minor texture components reappears in sample S5. The reason for this might be that there were pores and *a*-axial oriented grains in sample S5. It can be explained in detail in the discussion of the SEM observations below. Full width at half maximum (FWHM) of the out-of-plane texture was 1.328°, 0.829°, 1.116°, 1.132°, 1.306°, respectively. Therefore, the degree of texture was the best in sample S2 and the degree of texture did not vary significantly in the samples S3 and S4.

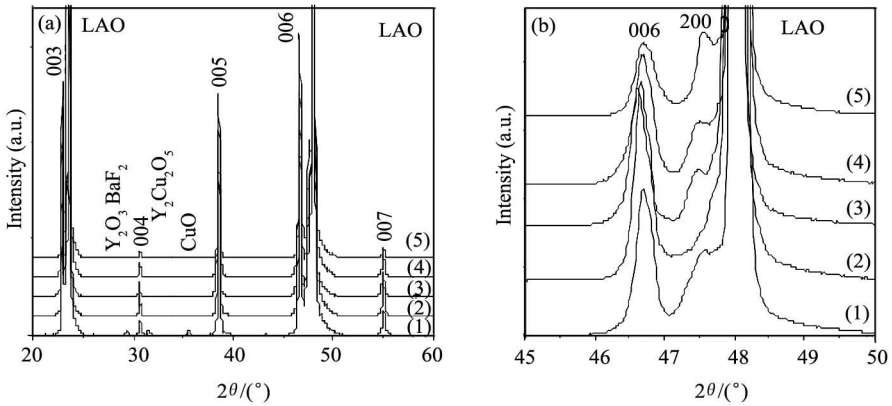

Fig.1 (a) XRD patterns of YBCO films fired at 820 °C in 2.6%–19.7% humidified N_2 gas mixed with 5vol.% O_2 and (b) Partially magnified image of Fig.1(a)

(1) 2.6%; (2) 4.2%; (3) 5.6%; (4) 7.3%; (5) 19.7%

Fig.3 shows surface morphologies of the YBCO films. It shows that all the films have a crack-free surface and are formed mainly by *c*-axis-oriented grains, i.e., grains in which the *c*-axis of the lattice is normal to the substrate. On the other hand, the surface morphology changes with humidity. There are a few *a*-axial-oriented grains in the films except sample S2, which is consistent with the results of XRD. For sample S1, the YBCO grains were very fine and contained big irregular particles. These particles were characterized by EDX to be CuO. For samples S2 and S3, the YBCO grains grew further and the film became denser. Some of big particles were characterized by EDX as YBCO in samples S2 and S3. On the other hand, similar microstructures including more pores and bigger size grains were observed for samples S4 and S5. Pores and *a*-axial-oriented grains have a negative effect to the texture of films, and that's why the minor texture components reappeared in pole figure of sample S5. Low humidity at 2.6% involves low conversion rates and not enough HF release; this might cause incompleted reaction or disorder (such as *a*-axial-oriented grains and pores)[10]. On the contrary, for samples S4 and S5, high conversion rates of reaction (1) was obtained

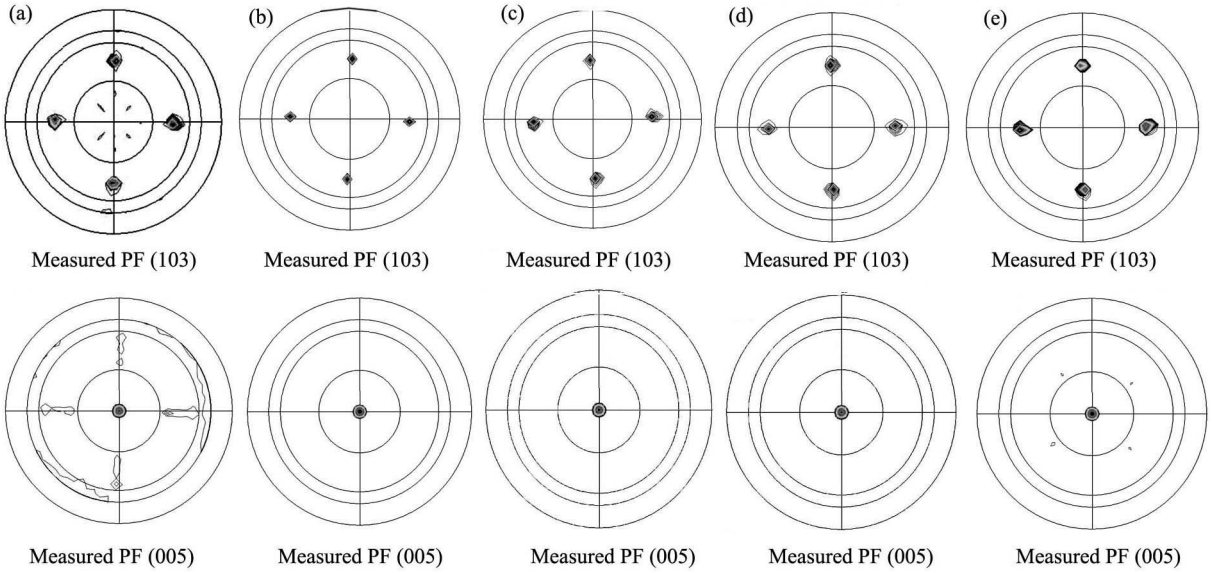

Fig.2 (103) and (005) pole figures of the films fired at 820 °C in 2.6% (a), 4.2% (b), 5.6% (c), 7.3 % (d), and 19.7% (e) humidified N_2 gas mixed with 5vol.% oxygen

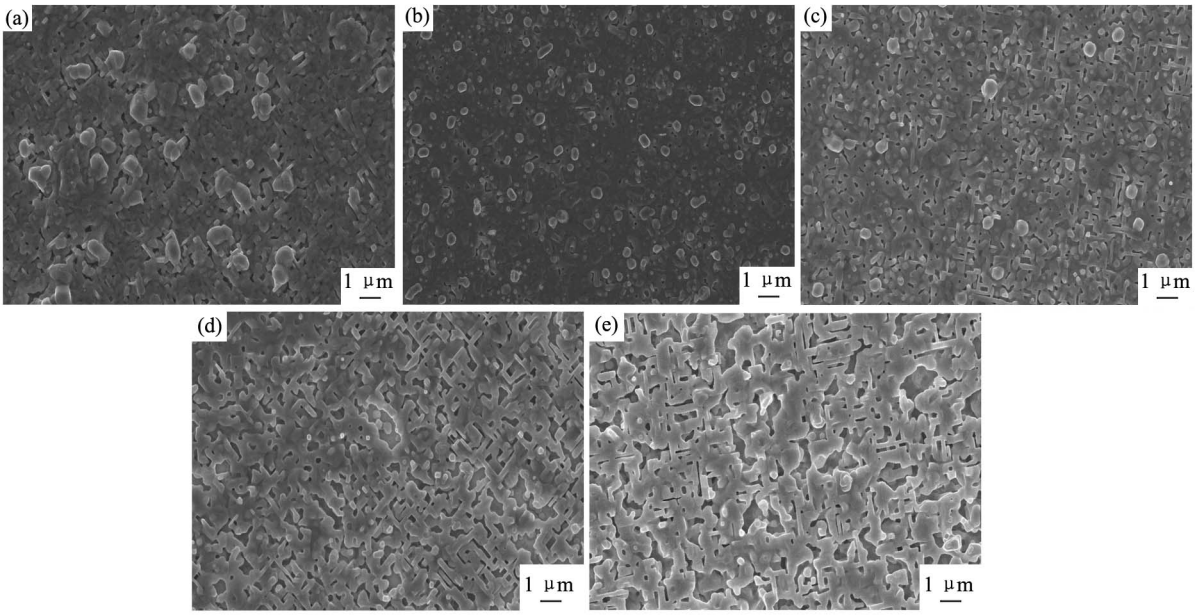

Fig.3 SEM images of YBCO films fired at 820 °C in 2.6% (a), 4.2% (b), 5.6% (c), 7.3% (d), and 19.7% (e) humidified N_2 gas mixed with 5vol.% oxygen

and resulted in distorted growth front producing disordered growth, i.e., when some *a*-axial-oriented grains nucleated in the film, there is not enough neighbouring *c*-axial-oriented grains to fill the gap between *a*-axial nucleation centers, and thus pores are formed.

Fig.4 shows the T_c and J_c values of samples S1-S5. With increasing humidity in range of 2.6%–19.7%, the corresponding T_c increased from 88 to 92 K (sample S2) and afterwards decreased to 90 K. High T_c values with a sharp transition range were obtained for all samples, suggesting that YBCO formed in all the films with high oxygen content. Similar trend of J_c values was also obtained. The J_c values increased with humidity and reached a peak of 3.3 MA/cm^2 in samples S1 and S2, decreased in samples S3, S4, and S5. The results were different with those obtained by Seok et al.[6] and Araki et al.[7]. We guessed this phenomenon might be caused by different gas atmospheres and firing temperature in firing process. YBCO is layered and current transmits along CuO layer. In the case of the existence of a-axial grains and pores, the transmission path is blocked and J_c value decreases. Based on the XRD pattern, PF and SEM images, it is possible that the highest J_c value is due to the existence of pure YBCO, strong biaxial texture, and large grain size with a dense microstructure. Therefore, the optimum humidity in the firing process at 820 °C is around 4.2% in this study.

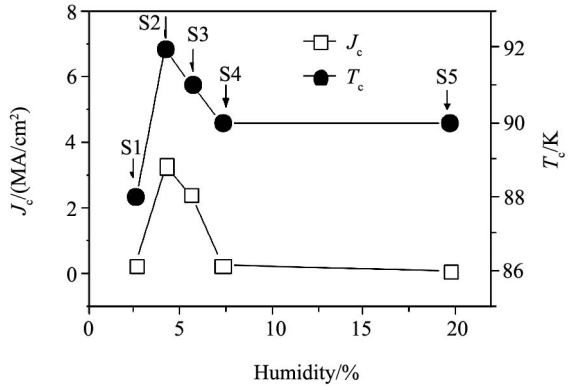

Fig.4 Dependence of critical current density and critical temperature on humidity

3 Conclusion

We investigated microstructure and superconducting properties on YBCO films fired at 820 °C in N_2 mixed with O_2 at different humidities (2.6%–19.7%). SEM study showed that all the YBCO films had crack-free surface. Because of incompleted reaction, second phases existed in the film; J_c and T_c were lower at the humidity of 2.6%. When the humidity was higher than 4.2%, there were more *a*-axial-oriented grains and more pores in the films caused by fast reaction; the values of J_c and T_c decreased with increasing humidity. YBCO films at the humidity of 4.2% had the best microstructure; and T_c and J_c reached 92 K and 3.3 MA/cm^2, respectively.

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