

Fabrication of Superconducting YBCO Thin Films on YSZ Substrates

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Abstract

High critical current density thick films of YBCO have been fabricated on yttria stabilised zirconia substrates. The quality and performance of the films was found to depend markedly on the processing of the initial starting powder used to form the printing ink for a fixed film processing cycle. Depending on the powder used, the critical transition temperature, $T_c(R=0)$, was found to vary between 87 and 91.5 K, and the critical current density was in the range 25 to 1200 A cm⁻² at 77 K in zero external magnetic field.

1. Introduction

Since the discovery of the high temperature superconducting YBCO material, many groups have attempted to produce high quality superconducting thick (5–50 μm) films on various substrates (Aponte and Octavio 1989; Barboux *et al.* 1988; Gupta *et al.* 1988; Lakshimi *et al.* 1989; Matsuoka *et al.* 1989). Unfortunately substrate/film interactions and incompatible thermal expansion coefficients have led most workers to use rapid, low temperature (~930°C) processing cycles which result in weakly interconnected granular films that are characterised by low critical current densities. It has been found recently (Bailey *et al.* 1989; Shields *et al.* 1990) that the use of yttria stabilised zirconia substrates allows for high temperature film processing above the peritectic decomposition temperature, without significant film contamination. Scanning electron microscopy and associated x-ray electron dispersive spectroscopy show that an inert BaZrO₃ barrier layer with dispersed CuO needles forms at the film/substrate interface, a result previously found by Tabushi and Utsumi (1988) and Abell *et al.* (1989), which inhibits atomic diffusion and film poisoning.

However, there are still other variable processing parameters that determine the quality of the resultant superconducting thick films. The results presented here show that the processing conditions used for the preparation of the initial precursor powder have a significant effect on the final superconducting properties of the films.

2. Experimental

The '123' YBCO starting powders were produced by first mixing stoichiometric amounts of commercially available Y₂O₃, BaCO₃ and CuO. The powder was

ball milled for approximately 24 hours to obtain a very fine homogeneous mixture. The powder was then divided into four batches and calcined in an alumina crucible by heating to 900°C at 1°C per minute, held at 900°C for batch times of 6, 12, 24 and 48 hours, to produce four differently reacted materials, and then cooled in air to room temperature at 1°C per minute. The four batches were then reground and sintered, the sinter cycle for each powder batch followed the original calcination cycle. The resultant powders were ring milled for 40 minutes and sieved through a fine mesh to produce a final powder with a particle size of approximately 1 μm . The powders were then mixed ultrasonically with appropriate quantities of triethanolamine ($\text{C}_2\text{H}_4\text{OH}$)₃N to produce the superconducting inks.

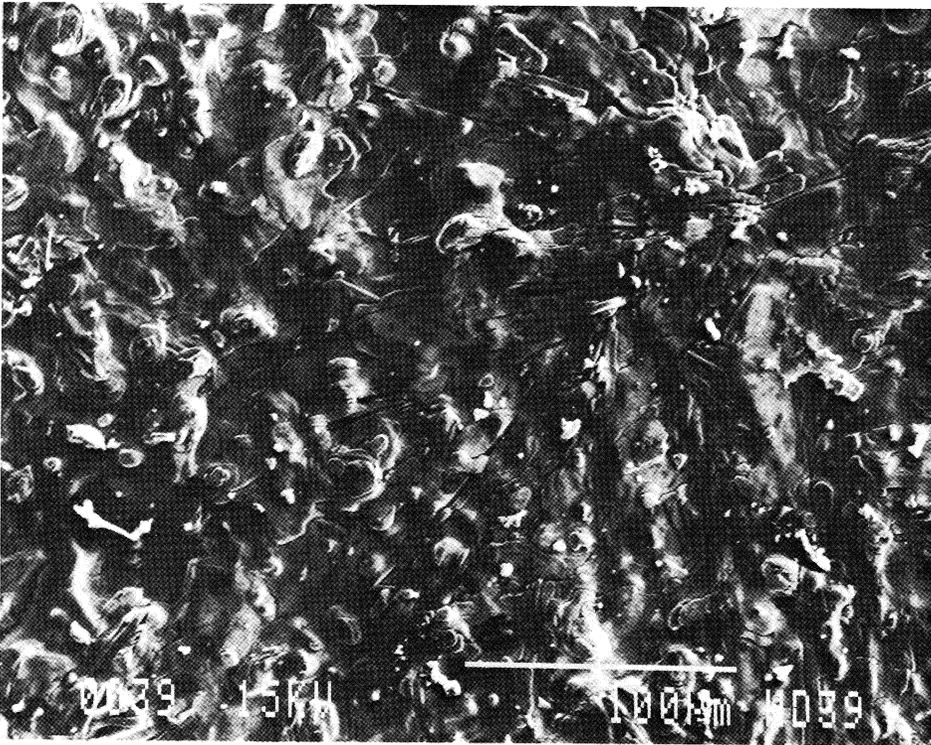


Fig. 1. SEM micrograph of a melt processed thick film using the 2x24 powder batch.

The four different inks, denoted by 2x6, 2x12, 2x24 and 2x48, were applied to the polished surfaces of YSZ substrates by carefully spreading the inks in one direction with a surgical blade. All films were initially approximately 40 μm thick and after drying at 200°C for 20 minutes, were sintered in air at 1015°C for 5 minutes before cooling to room temperature at 2°C per minute. Each film was found to be markedly reduced in thickness after heat treatment. Thickness measurements were performed with a scanning electron microscope by observation of cross sections through the layer. The conventional four-point probe technique and a continuous flow liquid nitrogen cryostat were used to determine the resistivity (ρ) versus temperature curves and hence the

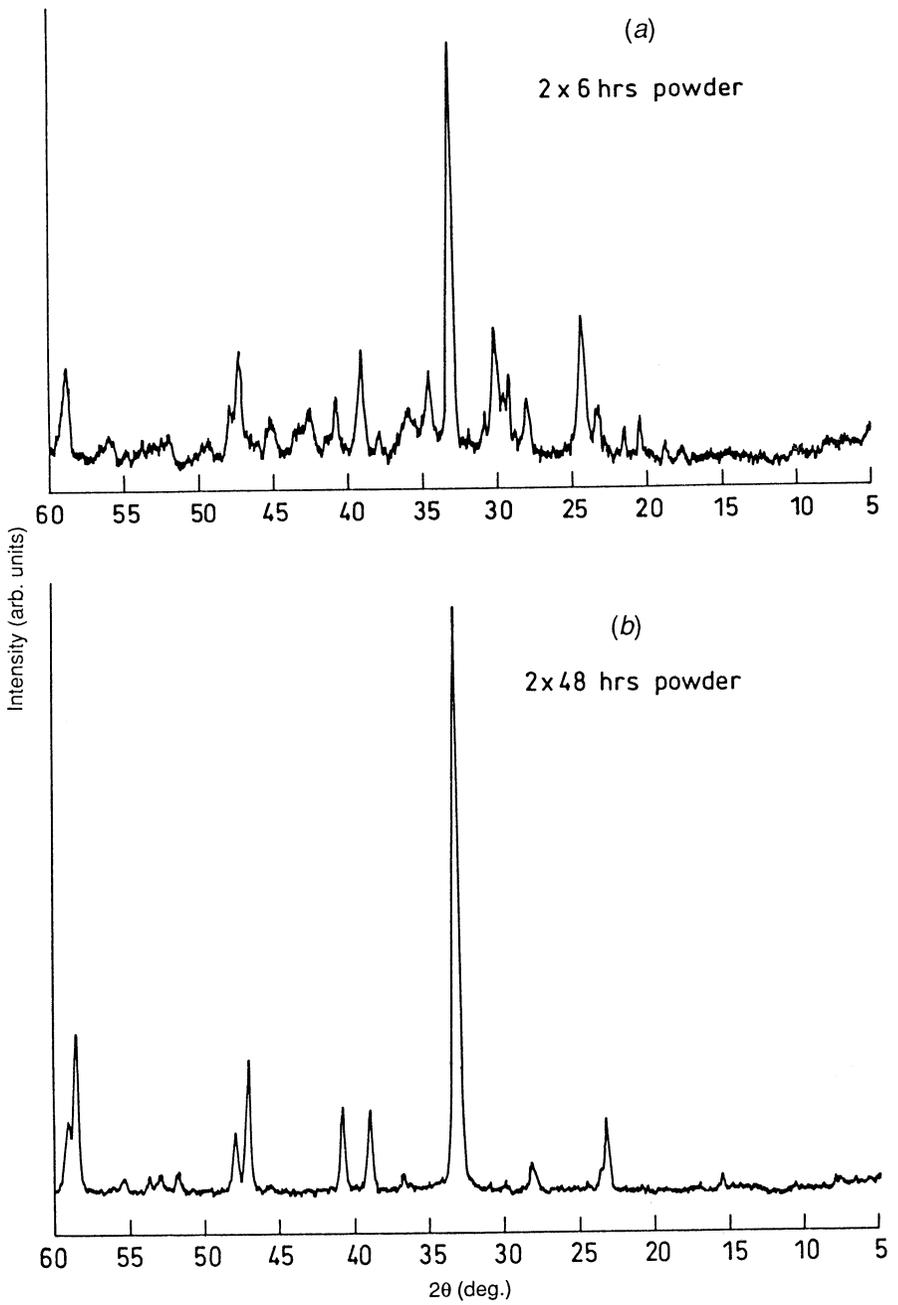


Fig. 2. XRD spectra for the (a) 2x6 and (b) 2x24 starting powder batches.

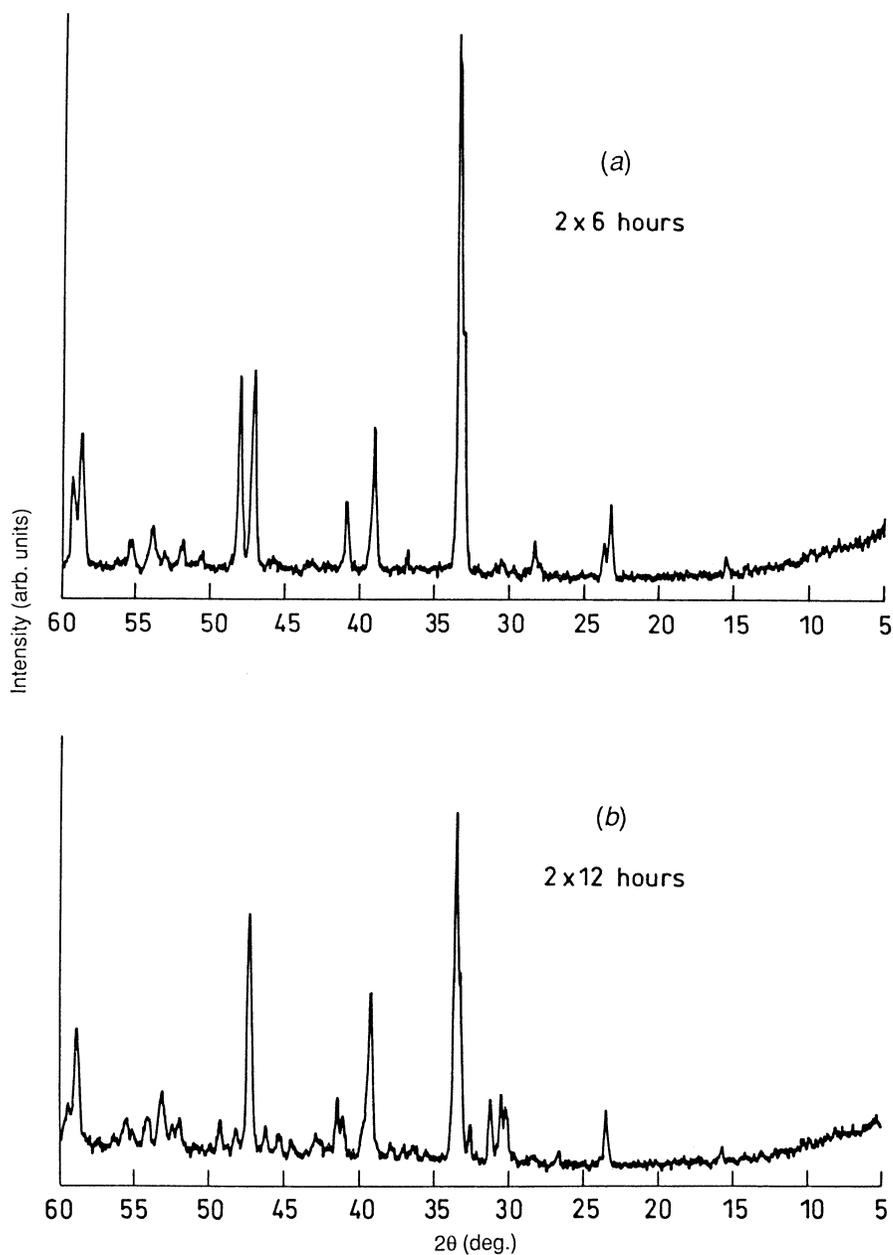


Fig. 3. XRD spectra for each film type showing increase *c*-axis texturing: (a) 2×6 powder batch, (b) 2×12 powder batch, (c) 2×24 powder batch, and (d) 2×48 powder batch.

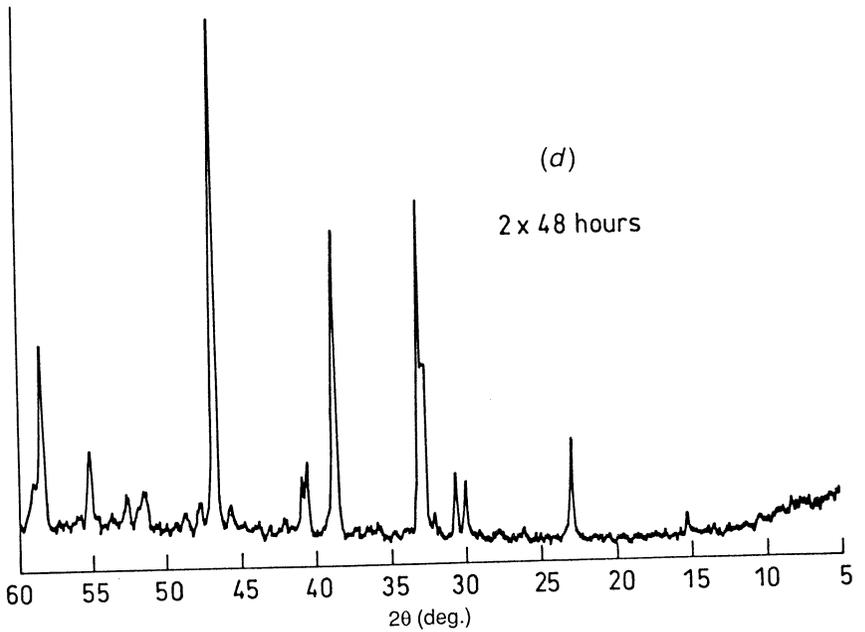
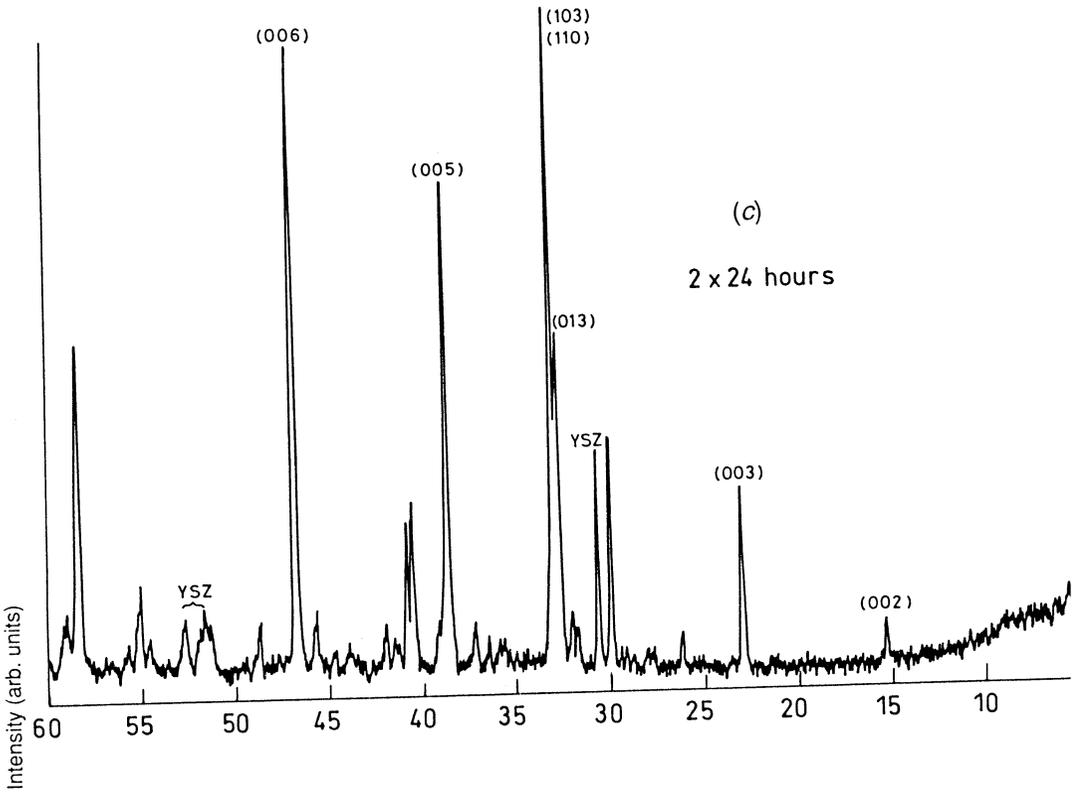


Fig. 3. (Continued)

critical temperature (T_c). The critical current density (j_c) of each film was determined at 77 K by immersing the sample in liquid nitrogen, determining the i - V characteristics and using the $1 \mu\text{V}/\text{cm}$ criterion. A number of films were measured for each powder batch to check the reproducibility of the data.

3. Results and Discussion

The thermal cycle used for the production of these thick films requires the use of a temperature in excess of the peritectic and therefore melt processing occurs (see Fig. 1). This processing has been found to lead to a number of advantages, including film texturing and the formation of an inert BaZrO_3 barrier layer, as detailed below. Fig. 2 shows the XRD spectra for the 2×6 and 2×24 starting powders. The 2×6 powder is only partly reacted and contains peaks from $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, Y_2BaCuO_5 , BaCuO_2 and Cu_2O phases. The 2×24 spectrum appears to consist of only an oxygen deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ phase as also is the case for the 2×48 powder. In the case of the 2×12 powder, the spectrum is very similar to that for 2×24 with a very small quantity of the Y_2BaCuO_5 phase being present.

Fig. 3 shows the XRD spectra of the films prepared from each powder batch. By comparing the intensity ratio of the 006 and 103 spectral lines for each spectrum, it is clear that c -axis texturing, normal to the film surface, is enhanced with increased reaction time of the precursor powder used to manufacture the inks. The temperature variation of the resistivity, near the superconducting transition temperature, for each film type is shown in Fig. 4.

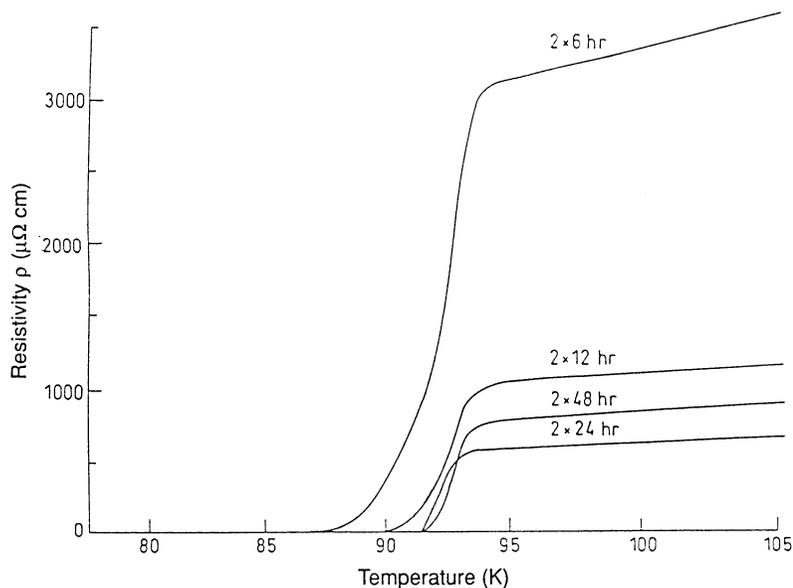


Fig. 4. Temperature variation of resistivity, near the transition temperature, for each film type.

Table 1 tabulates the resistivity value at 100 K, the transition temperature T_c and the critical current density, j_c , for each film type. A range is given for each j_c value listed and represents the variation in this quantity found for

a number of films prepared from the same starting powder processed under identical conditions. The resistivity and T_c values did not show this film-to-film variation. Clearly both T_c and j_c increase and ρ decreases with increasing powder processing times for the first three batches. Films fabricated from the 2×48 powder batch do not support the trend and while the texturing figure of merit continues to increase both the resistivity and the critical current density deteriorate (resistivity increase, j_c decreases), indicating that factors other than the degree of texturing are involved in determining the critical current density in these films.

Table 1. Film characteristics for various processing conditions

Powder batch	T_c (K)	Resistivity at 100 K ($\mu\Omega$ cm)	j_c (A cm ⁻²) at 77 K	Barrier layer thickness (μ m)	YBCO film thickness (μ m)	c -axis texturing I_{006}/I_{103}
2×6 hr	87	3400	25–35	6·3	3·4	0·37
2×12 hr	90	1120	80–100	8·5	11·8	0·67
2×24 hr	91·5	640	750–1200	9·6	15·0	1·05
2×48 hr	91·5	853	200–300	≤0·2	14·0	1·52

Fig. 5 shows two edge-on SEM micrographs which indicate typical dimensions for the YBCO film and the inert barrier (buffer) layer. This barrier layer forms during melt processing of the film and has been found to have the composition BaZrO₃ with fine CuO needles dispersed throughout, a result found by Tabushi and Utsumi (1988) and Abell *et al.* (1989). Typical YBCO and BaZrO₃ film thicknesses are given in Table 1. For the first three powder batches the inert barrier layer increases slowly with increasing initial powder reaction time. For the 2×48 powder, however, the barrier layer could not be detected under the experimental conditions suggesting a thickness ≤0·2 μ m. Therefore, under these conditions the barrier is too thin to inhibit atomic diffusion and thus partial film poisoning occurs with a resultant reduction in the electrical transport property. It is assumed that this layer is formed by reaction between the YSZ substrate and the liquid phases that are present during the melt processing cycle. The dependence on reaction time which has been observed above clearly indicates that the residual phases present in the precursor powders may play an important role in both the film formation and the development of the barrier. The longer the reaction time at 900°C for the starting powders, the smaller the amount of residual products, the powder eventually becoming essentially pure '123'. The barrier layer is consequently relatively thinner for these powders, in agreement with the data shown in Table 1. The observed j_c variation is explained by taking into account the c -axis texturing data shown in Table 1. It is now accepted that j_c measured along the a - b plane is significantly higher than that along the c -direction. Thus j_c should increase with increased texturing and the results shown in Table 1 indicate this trend, except for the 2×48 film type. This film has the highest c -axis texturing but the smallest inert barrier and must be partially poisoned. On the other hand the 2×6 film type has the thickest barrier layer, but the lowest j_c value, an effect which may be explained in terms of the

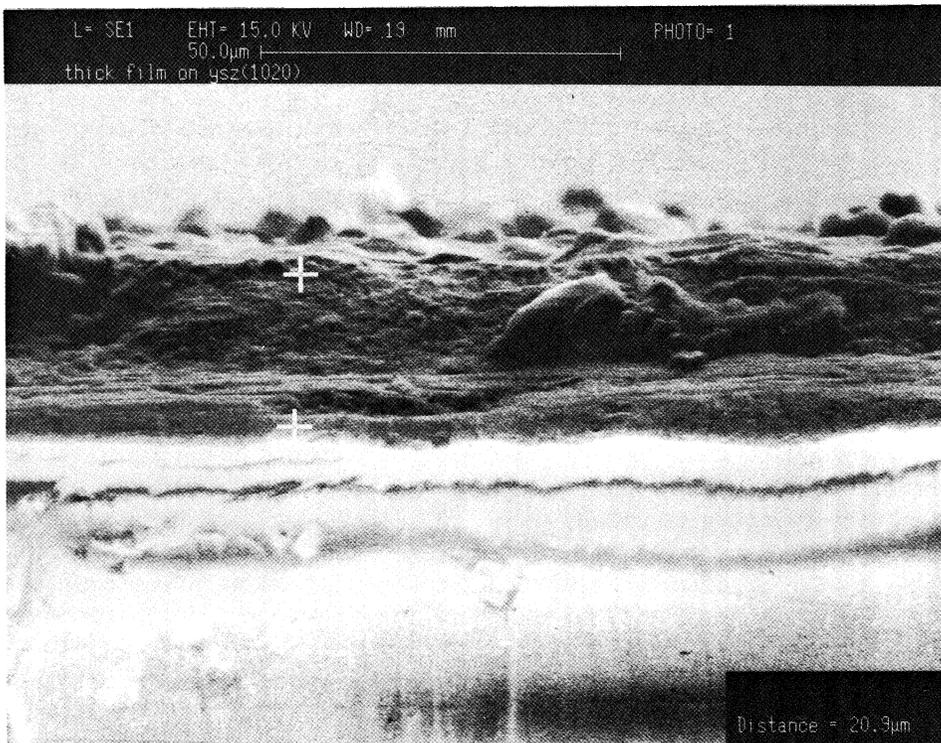
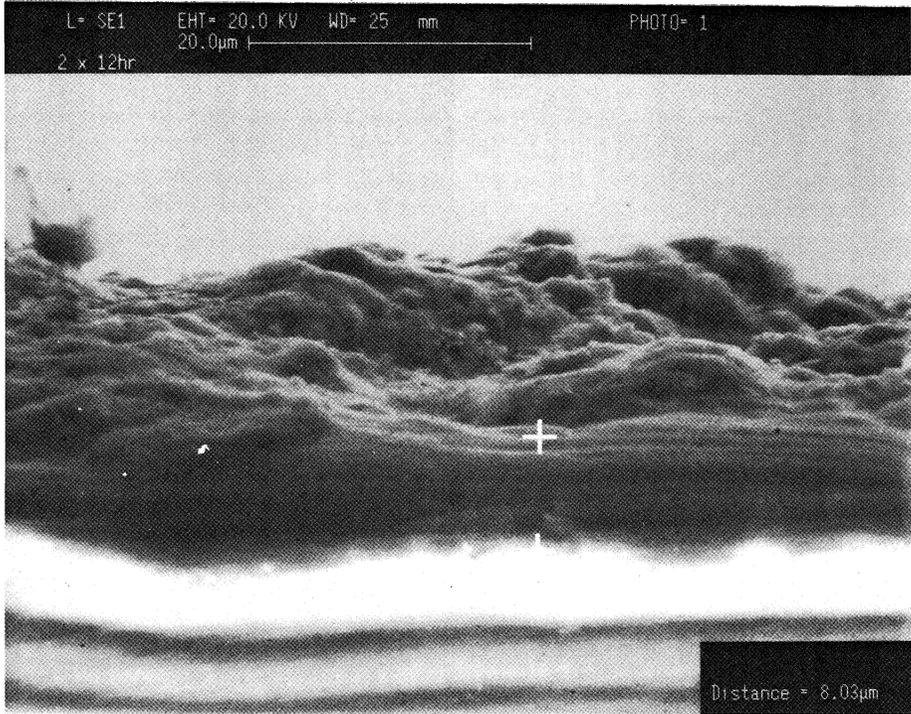


Fig. 5. Edge-on SEM micrographs showing typical thicknesses for the YBCO film and the inert barrier layer: top, 2x12 powder batch and bottom, 2x24 powder batch.

poor film texturing and a YBCO film thickness of dimension comparable to the grain size.

To further improve the properties of these films, work is now in progress to increase film texturing and to change the nature of the intergranular contacts to improve grain connectivity.

4. Conclusions

High critical current density thick films of YBCO can be fabricated on YSZ substrates, if the initial starting powder used to form the printing ink, is calcined and sintered at 900°C for 24 hours, respectively. The critical transition temperature for these films was 91.5 K and j_c varied in the range 750–1200 A cm⁻² at 77 K in zero external magnetic field. The thermal cycle for the production of these films required the use of temperatures in excess of the peritectic and therefore involved melt processing. This has a number of advantages, including film texturing and the formation of an inert BaZrO₃ barrier layer which has fine CuO needles dispersed throughout. This layer appears to prevent atomic diffusion and film poisoning provided that its thickness is of the order 8 μm or more.

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