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SYNTHESIS OF C-ORIENTED $YbBa_2Cu_3O_{7-\delta}$ FILMS ON SINGLE AND POLYCRYSTALLINE SUBSTRATES BY OXIDATION OF LIQUID ALLOYS

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ABSTRACT

Textured superconducting films of $YbBa_2Cu_3O_{7-\delta}$ supported on single and polycrystalline substrates were prepared by oxidation of a liquid precursor alloy. The substrates were coated by dipping them into a molten alloy ($YbBa_2Cu_3$, m.p. ~870°C), withdrawing them from the melt, then oxidizing the adhering liquid alloy layer to the corresponding oxide phase, i.e., $YbBa_2Cu_3O_{7-\delta}$. Samples prepared in this way exhibited a superconducting transition at ~80 K following annealing in pure O_2 at 500°C. With $SrTiO_3$ (100) and MgO (100) substrates, evidence was seen for the epitaxial growth of $YbBa_2Cu_3O_{7-\delta}$ crystals having their **c**-axis parallel to the [100] direction of the substrate. For polycrystalline MgO, x-ray diffraction and microstructural examination showed that the high-T_c crystallites in the films were also oriented with their **c**-axis perpendicular to the substrate surface, but the **a** and **b** axes directions were randomly oriented rather than epitaxial.

INTRODUCTION

It has been proposed [1-5] that an alternative route to the synthesis of high-T_c superconductors, involving oxidation of metallic precursor alloys having appropriate compositions, might offer attractive advantages over more conventional ceramic processing methods. Chen et al. [6,7] first showed that it is possible to induce an epitaxial growth of $YbBa_2Cu_3O_{7-\delta}$ films (~2 µm thick) by oxidation of a liquid precursor alloy supported on $SrTiO_3$ (100) substrates. The formation of superconducting $YbBa_2Cu_3O_{7-\delta}$ from the melt is reported to improve the homogeneity of the resulting film. Grain boundary weak links also were greatly minimized by the preferential alignment of grains parallel to the **a-b** conduction planes. In this paper, we describe the preparation of textured films of $YbBa_2Cu_3O_{7-\delta}$ on both single-crystal and bulk polycrystalline substrates, by oxidation of a liquid alloy precursor.

EXPERIMENTAL PROCEDURE

The starting alloy was prepared by induction melting of a stoichiometric mixture of the constituent metals ($YbBa_2Cu_3$). The substrates used were $SrTiO_3$ (100) MgO (100), and slices cut from hotprocessed polycrystalline MgO. Their dimensions were typically 10 x 10 x 0.5 mm. Prior to film preparation, the substrates were polished and cleaned in an ultrasonic bath. In preparation for dip-coating, alloy specimens in the form of ingots weighting ~45 grams were placed in an alumina crucible, heated in a stainless steel vessel surrounded by a vertical resistance furnace to temperatures ranging from 960°C to 975°C under a UHP argon atmosphere, and held for 30 min. A substrate specimen, supported above the alloy crucible in a specially designed dip assembly [8], was immersed into the molten alloy ($YbBa_2Cu_3$, m.p. ~870°C), allowed to sit for about 10 seconds to assure complete wetting, and withdrawn from the melt. (The dip assembly provided a means of parting the dross layer on the liquid alloy surface so that only dross-free liquid touched the surfaces of the substrates.) The adhering metal was immediately oxidized by directly introducing oxygen into the dip-coating apparatus. Typical oxidations were conducted under flowing oxygen at the same temperature used for the dip and lasted ~30 min. After oxidation, the temperature was lowered to 500°C, where samples were oxygenated (in pure oxygen) for about 16 hours, then furnace-cooled to room-temperature. A more detailed description of the apparatus and procedures used to prepare $YbBa_2Cu_3O_{7-\delta}$ films by liquid alloy oxidation will be presented elsewhere [8,9].

X-ray diffraction was performed with filtered Cu $K\alpha$ radiation using a Philips diffractometer. The resulting films were also examined by scanning electron microscopy on a JEOL 35U equipped with an energy-dispersive x-ray analyzer. Resistivity measurements were carried out on as-prepared (unpatterned) films using a standard four-probe dc method employing silver paint contacts.

RESULTS AND DISCUSSION

The oxidized films, typically 10 μm thick for single-crystal substrates and 20 μm thick for polycrystalline substrates, had smooth surfaces and exhibited a uniform coloration. XRD patterns of the film surfaces on both single-crystal and polycrystalline substrates (see Fig. 1) were dominated by the {00l} peaks of orthorhombic $YbBa_2Cu_3O_{7-\delta}$. The lattice parameters for the film on the polycrystalline MgO were essentially the same as those obtained on single-crystal substrates, presumably due to the similar synthesis/processing conditions. A peak located at $2\theta = 33°$, corresponding to the most intense peak of randomly oriented $YbBa_2Cu_3O_{7-\delta}$, appears for both types of samples but is slightly more prominent for the polycrystalline substrate as can be seen in Fig. 1. Small amounts of impurity phases, mainly $BaCuO_2$ and Yb_2BaCuO_5, are also present (more in the case of polycrystalline substrates than single-crystals).

The results obtained with the polycrystalline MgO substrates suggest the potential for a new approach to the preparation of oriented films without exclusive use of single-crystal substrates. In this case, preferential **c**-axis orientation is most probably due to rapid anisotropic crystallization of $YbBa_2Cu_3O_{7-\delta}$ caused by a tendency of all available MgO facets to nucleate **a-b** plane growth in preference to **a-c** or **b-c** growth. It is possible that the rapid oxygen diffusion and phase formation, occurring at kinetically favorable liquid metal/solid oxide phase boundaries, facilitate this anisotropic growth.

SEM examinations of the films revealed a uniform microstructure of $YbBa_2Cu_3O_{7-\delta}$ crystals with some dispersed impurity phases. Films on single-crystal $SrTiO_3$ (100) and MgO (100) grow in a regular rectangular pattern with platelet dimensions of ~15 x 15 μm that corresponds to the {00l} surface of $YbBa_2Cu_3O_{7-\delta}$ (Fig. 2a and 2b). Some cracks were observed in the surface view, and separations among the platelets were systematically present. However, transmission electron microscopy (TEM) reveals that the grains are compact and uniformly interconnected in the vicinity of the film/substrate interface [9]. This result is comparable to observations by Chen et al. [6] for $YbBa_2Cu_3O_{7-\delta}$ films supported on single-crystal $SrTiO_3$ (100). SEM results for the polycrystalline MgO substrate showed that the **a-b** platelets are still present, confirming a growth pattern favoring the {00l} planes of orthorhombic $YbBa_2Cu_3O_{7-\delta}$ (Fig. 2c). However, the grain dimensions (typically ~4 x 4 μm) are about 4 times smaller than those observed for films nucleated on MgO (100), and are completely randomly oriented in terms of **a** and **b** axes direction even though the **c**-axis is predominantly perpendicular to the substrate surface. The randomly oriented a-b platelets are believed to be a consequence of the polycrystalline nature of the substrate.

The superconducting transitions for the best films prepared in this study begin at around 80 K. This value is comparable to that reported by Chen et al. [6] for films grown on single-crystal $SrTiO_3$ (100), but is lower than that (T_c = 90 K) obtained for single-crystal $YbBa_2Cu_3O_{7-\delta}$ [10]. Approximate critical current densities have also been determined for several samples (at 56 K and zero field for films on $SrTiO_3$ (100) and MgO (100) and at 50 K and zero field for films on polycrystalline MgO substrates). Using the critical current corresponding to the inflection point in the current-voltage curve or a voltage criterion of ~1 μV/cm gives J_c values of ~1000 A/cm^2 and ~500 A/cm^2 for films supported on single-crystal $SrTiO_3$ and MgO, respectively, and ~130 A/cm^2 for the film on polycrystalline MgO. These values are substantially lower than ones reported by Chen et al. [6] for oxidized alloy films on $SrTiO_3$ (100) substrates or for samples prepared by melt-textured-processing [11]. However, our J_c values, which were measured on unpatterned films, should be more representative of the bulk properties of oxidized alloy films than those of Chen et al. [6] for a restricted (patterned) area ~150 μm wide and ~2 μm thick.

The relatively low T_c value for as-prepared samples is most probably due to incomplete oxygenation of the orthorhombic $YbBa_2Cu_3O_{7-\delta}$, caused by slow oxygen diffusion along the **c**-axis, i.e., relative to that in the **a** and **b** axes directions [12]. The larger **c**-spacing (**c** = 1.168 nm) observed in these samples compared to the 90 K $YbBa_2Cu_3O_{7-\delta}$ (**c** = 1.165 nm) [10] seems to be related directly to the oxygen-deficient nature of the samples. The incomplete oxygenation may also be connected with the presence of the second phases which impede inward oxygen diffusion.

The low J_c values are undoubtedly caused by the crack development observed in SEM micrographs of the film surface. Of course, the presence of impurity phases could also be contributing to the diminished electrical performance. Thinning of the liquid alloy layer prior to oxidation (to produce thinner films of high-T_c oxides) should help to alleviate crack formation.

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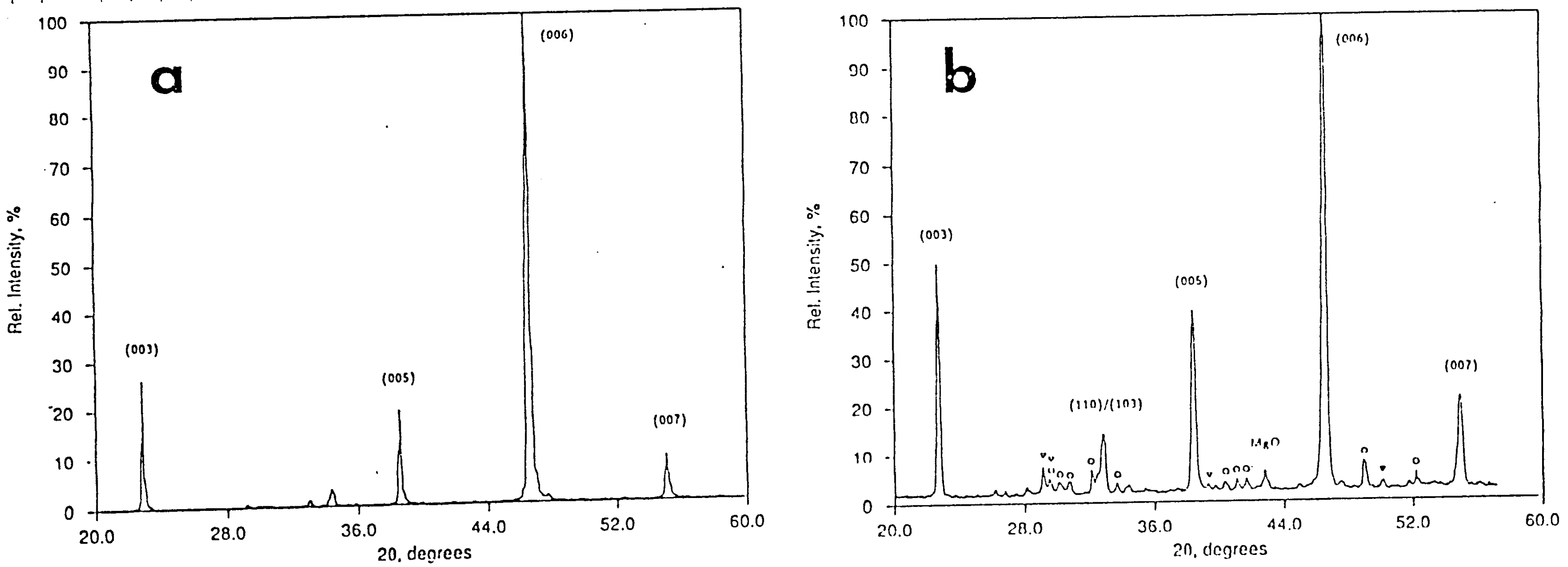

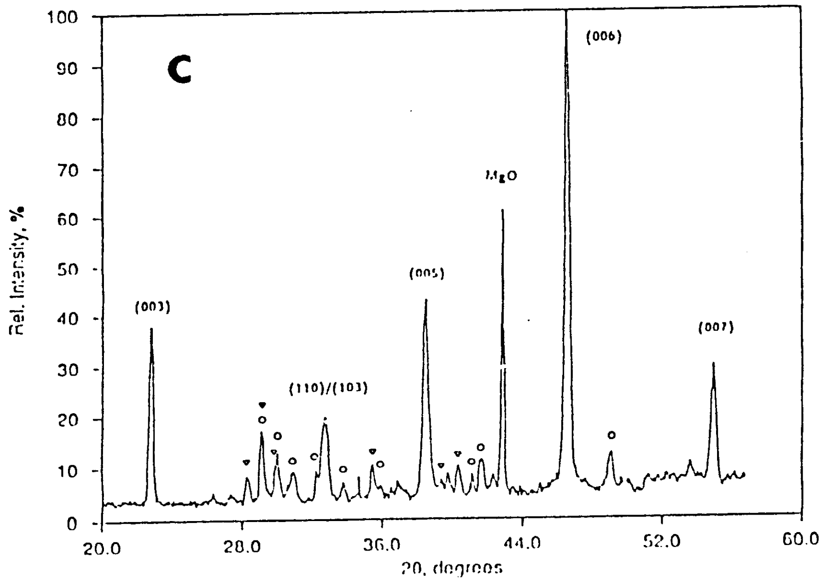

Figure 1. X-ray diffraction patterns of $YbBa_2Cu_3O_{7-\delta}$ films prepared by oxidation of a liquid alloy precursor: (a) on $SrTiO_3$ (100), (b) on MgO (100), and (c) on polycrystalline MgO. ▽ = $BaCuO_2$, ○ = Yb_2BaCuO_5.

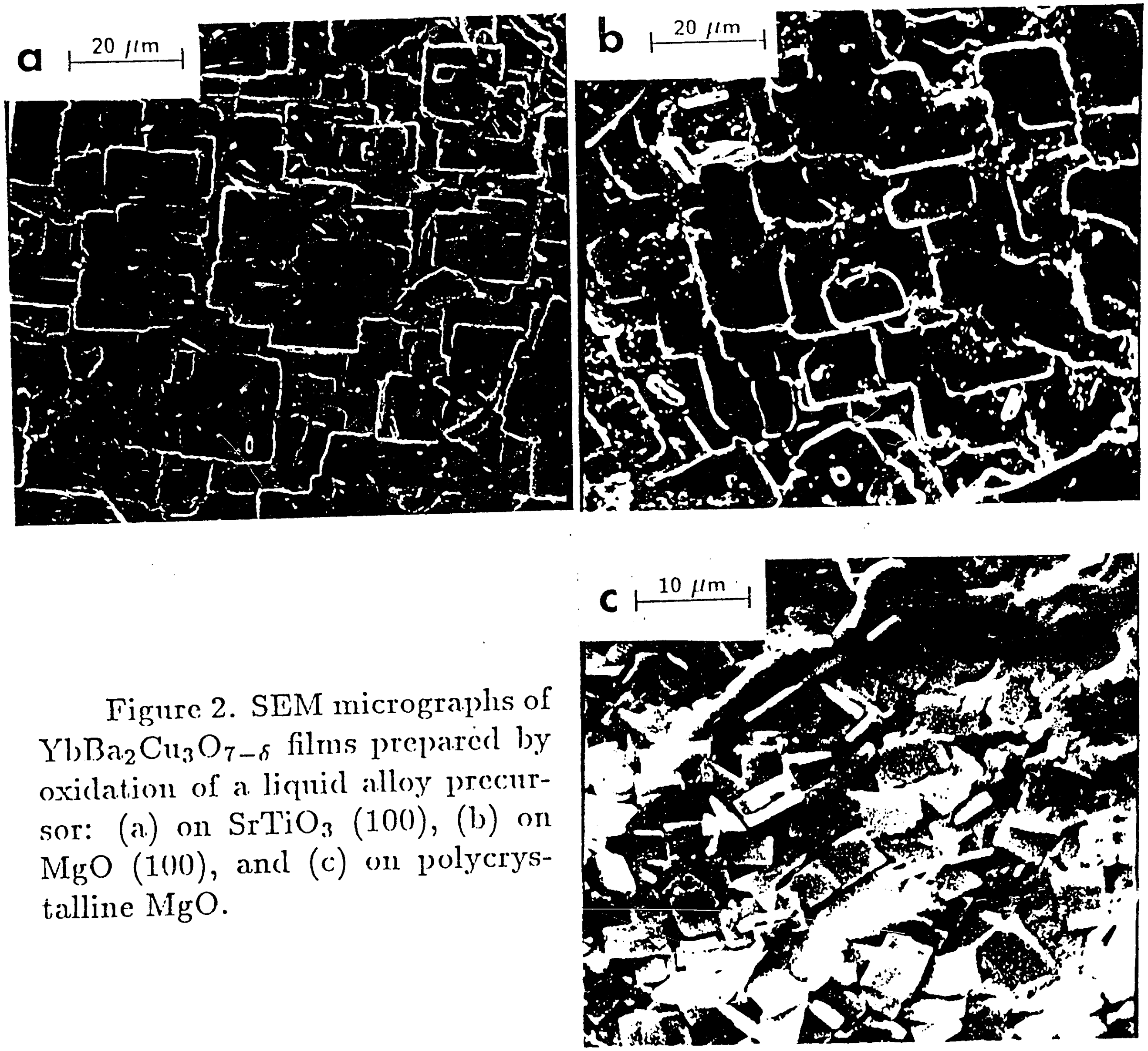

Figure 2. SEM micrographs of $YbBa_2Cu_3O_{7-\delta}$ films prepared by oxidation of a liquid alloy precursor: (a) on $SrTiO_3$ (100), (b) on MgO (100), and (c) on polycrystalline MgO.

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