

REACTIVE GROWTH OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ LAYERS ON Y_2BaCuO_5 SUBSTRATES

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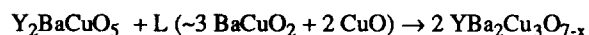
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Abstract

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thick films were grown via a solid/liquid reaction between Y_2BaCuO_5 and a mixture of $3 \text{BaCuO}_2 + 2 \text{CuO}$. The morphology of the 123 films was found to be related to the microstructure of the parent solid phase. The reaction kinetics has been investigated and the growth mechanisms are discussed in relation with the density of the substrates.

1. Introduction

This work investigates the formation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (123) through a solid/liquid diffusion process. The diffusion couple is composed of Y_2BaCuO_5 (named the green phase or 211) as the high melting point component, and a mixture of $3 \text{BaCuO}_2 + 2 \text{CuO}$, which is liquid at the reaction temperature. The 123 phase is formed by the peritectic reaction:



This reaction also occurs when a stoichiometric 123 phase is cooled from a temperature above the peritectic temperature. It is exploited in various processes widely studied recently to produce textured superconducting ceramics (reviewed in references 1 and 2). However, the reaction mechanisms are not yet fully understood. While it is most often assumed that 211 acts as heterogeneous nucleation sites for the 123 grains (3), some works point out results suggesting a dissolution of 211 in the liquid (2, 4) and the nucleation of 123 particules in the melt (4, 5).

Several authors have described the production of 123 films by solid/liquid reaction (6-10). This process allows to avoid the contamination of the superconducting phase by the substrate supporting the film, since this substrate is stable with respect to 123 according to the equilibrium phase diagram. The layers produced were dense and superconducting.

The present work aims at elucidating the mechanisms of the growth of the superconducting films synthesized by this solid/liquid reaction route. The final objective is to design a process which would make possible the production of textured ceramic layer by taking advantage of the presence of the liquid phase. Different substrates were prepared by sintering 211 powder. They were allowed to react with the liquid Ba-Cu-O mixture. The samples were characterized by XRD, EPMA, SEM and optical microscopy. The

observations were linked to the density and the microstructure of the substrates.

2. Samples preparation

The 211 phase and BaCuO_2 were synthesized in the solid state from adequate molar proportions of BaCO_3 , CuO and, for 211, Y_2O_3 powders. The powders were ball-milled and calcinated at 930°C for 20 to 90 hours with intermediate grinding steps. The Ba-Cu-O mixture was obtained by mixing BaCuO_2 and CuO in molar ratio 3:2 during 5 hours.

The 211 powder was subsequently compacted by uniaxial pressing under 300 to 750 MPa or by isostatic pressing under 140 MPa. Uniaxial pressing provided a pellet ready to be sintered whereas the cylinder bars obtained by isostatic pressing were heat treated for 5 h at 1000°C in order to allow machining of disk-shaped pellets whose surface was smoothed on abrasive paper before subsequent sintering. These 211 pellets were sintered between 1000 and 1230°C during 10 to 90 hours.

For the preparation of 123 films, 0.2 mm-thick pellets of the Ba-Cu-O mixture were prepared by uniaxial pressing and deposited on the surface of the sintered 211 disks. The two components were reacted during 5 hours in flowing oxygen at a temperature of 980°C . For the $3 \text{BaCuO}_2 + 2 \text{CuO}$ mixture, this temperature is higher than the liquidus temperature which, according to the published phase diagrams, is around 950°C . After this heat treatment, the samples were cooled at a rate of $1^\circ\text{C}/\text{min}$ down to 450°C . A dwell of 10 hours at this temperature was allowed in order to obtain the proper oxygen content in the 123 phase.

For determining the growth kinetics, the same experiments were conducted using various durations for the dwell at 980°C and a faster cooling rate of $8^\circ\text{C}/\text{min}$.

3. Results and discussion

3.1. Densification of the green phase substrates

The density of the powder samples compacted by uniaxial pressing reached 3.2 gcm^{-3} , i.e. about 50% of the theoretical density of 6.197 gcm^{-3} . A higher density amounting to 66% of the theoretical density was obtained in the disks prepared by isostatic pressing. A minimum duration of heat treatment of 30h at 1150°C was required to achieve a density of about 85%. The average grain size amounted then to about $20 \mu\text{m}$. Relative densities of up to 90% were obtained when increasing the sintering time to 90h or when increasing the sintering temperature to the range $1200\text{-}1230^\circ\text{C}$. These samples presented a much larger average grain size of 50 to $150 \mu\text{m}$ whereas most of the porosity was closed and trapped inside the grains. XRD diagrams of the surface of the substrates corresponded to pure 211 phase whatever the conditions of sintering.

3.2. Microstructure of the 123 layers formed by solid/liquid reaction

After the diffusion reaction, a continuous film of 123 was observed on all substrates. While containing some cracks, this film was dense. Apart from the presence of some aggregates of CuO, the elements ratio Y:Ba:Cu measured through the layer was round 1:2:3. In all samples, the observation of sets of twin boundaries in numerous grains attested that the tetragonal \rightarrow orthorhombic phase transition had occurred. This fact is confirmed by XRD. Resistivity measurements give T_c values near 89K, with a transition width of about 3K.

The morphology of the superconducting layer was strongly influenced by the microstructure of the 211 substrates. On the less dense substrates which contained an open porosity of 10% or more, the liquid infiltrated the matrix, leading to the formation of a network of 123 phase inside the bulk of the 211 substrate. Nevertheless, in this case, we observed on the surface of the substrate the formation of a layer of 123 grains forming a rather regular film of about $20 \mu\text{m}$ thickness. In several cases, XRD diagrams showed evidence of a strong crystallographic orientation in this layer, with the c-axis of the 123 particules perpendicular to the surface (Figure 1).

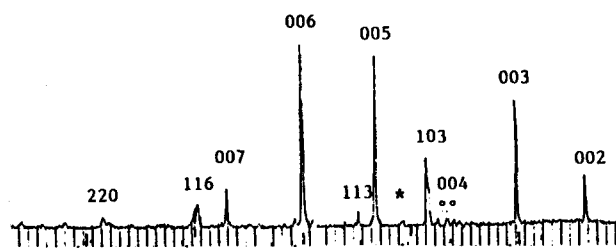


Figure 1. Indexed XRD diagram of the surface of a 123 film grown on a 211 substrate containing an open porosity of 17%. (* CuO, ° $BaCuO_2/Y_2BaCuO_5$)

On substrates sintered for a long time or at high temperature and presenting thus large grain size and closed porosity, a continuous layer of 123 was observed, the thickness of which varied from 20 to $100 \mu\text{m}$ (Figure 2). This film was surmounted in several places by a porous overlayer of $BaCuO_2+CuO$. The 123 phase was mainly composed of grains having the shape of platelets 20 to $50 \mu\text{m}$ in length. In most samples, these ones tended to be aligned perpendicularly to the substrate surface, giving the appearance of a columnar structure (Figure 2). It is generally admitted that, in high aspect ratio grains of 123, the basal planes (001) are parallel to the elongation direction (11). However, XRD diagrams taken on the top of these sample after removal of the overlayer of $BaCuO_2+CuO$ did not show significant changes of the peak intensities which would reflect the presence of a crystallographic texture associated with this morphological alignment. This point needs to be further elucidated.

A similar alignment of the 123 grains in the normal direction can be observed in pictures of 123 layers grown by solid/liquid diffusion, which have been published by other authors (6, 7, 10). A quite different morphology was obtained by Freeman and coworkers (8, 9). In that work the 123 layers grown onto 211 were divided into two or three regions where the size and orientation of the grains varied (as well as the overall composition) whereas a perpendicular alignment of small columnar grains of 123 was also observed close to the interface with the 211 phase. No specific texturing was reported in any of these works.

3.3. Kinetics of growth

The kinetics of the growth of the 123 layer was studied on the 211 substrates obtained by sintering at 1150°C during 90h. The growth of the film in the solid/liquid system appeared very fast. After a few minutes above 980°C , a layer of fine platelets of about $20 \times 3 \mu\text{m}$ size has been formed (Figure 3). The grains stood perpendicular to the substrate surface. Many pockets of Ba-Cu-O mixture were observed between the 123 grains.

The 0.2 mm -thick disks of Ba-Cu-O reactant had been fully consumed after a reaction time of 20h. Then, the 123 platelets appeared to have also thickened by sintering during the long heat treatment (Figure 4).

The fast growth of 123 has been already observed by Chen and coworkers (5). They demonstrated that 123 recrystallizes from a melt in a very short time, especially at temperature around 940°C .

3.4. Mechanisms of growth

The growth mode of the 123 phase on the dense substrates confirms that heterogeneous nucleation occurs on the 211 phase. If the density of nuclei is high, the sterical obstruction along the interface allows the grains to grow only in the normal direction. The dissolution of



Figure 2. Optical micrograph of the cross section of a 123 layer grown during 5 h on a substrate sintered 30h at 1150°C and 30h at 1210°C.

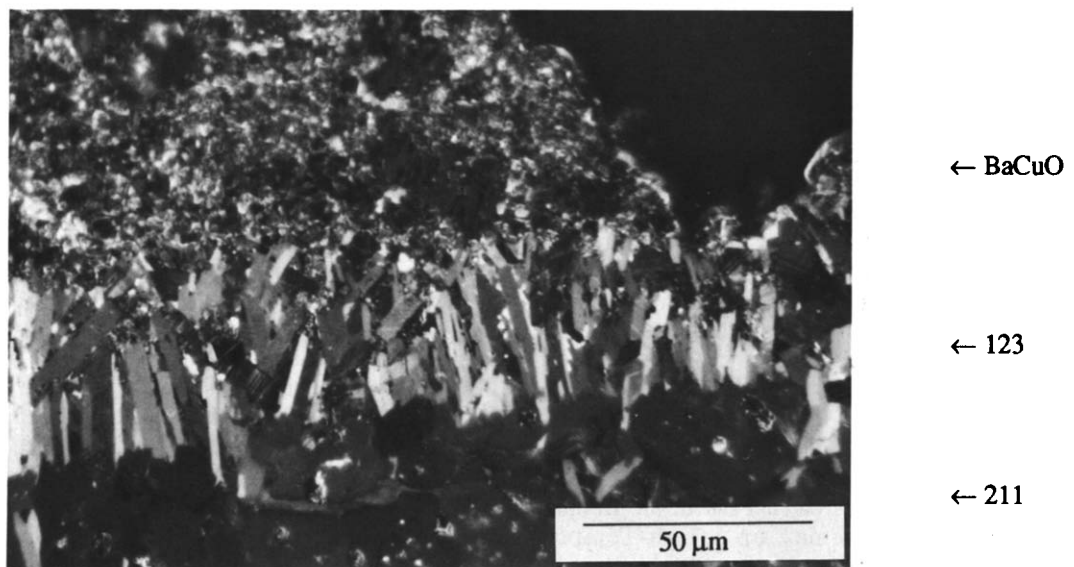
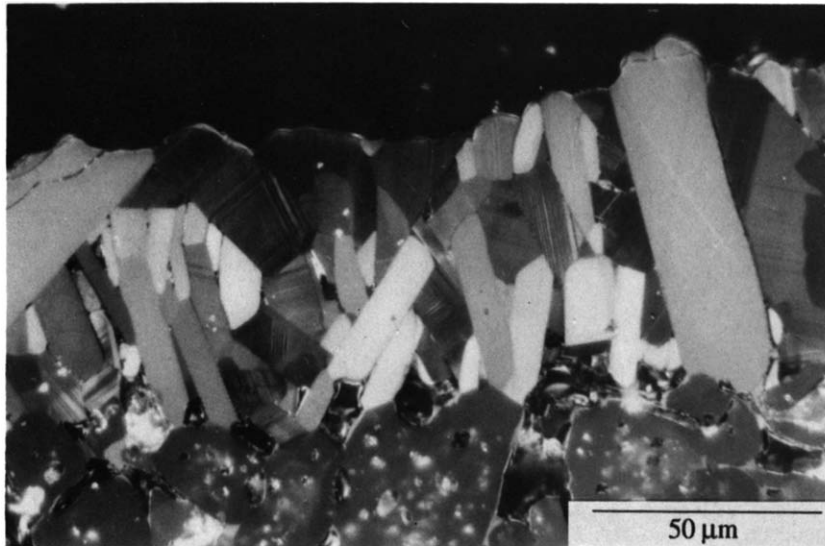


Figure 3. Micrograph of the cross section of a sample reacted 5 minutes at 980°C. Substrate sintered 90h at 1150°C.

211 inside the melt allows an easy diffusion path for the elements. This could explain the rapid growth of the 123 platelets. The liquid filled space between the grains closes progressively and, finally, the growth of the film becomes much slower when no direct contact remains between the liquid phase and the 211 phase. As no preferential orientation of the 211 grains has been detected in the sintered substrates, the alignment of the 123 platelets in the film indicates the absence of mutual

orientation between the 123 nuclei and the 211 nucleation sites.

Concerning the strong orientation of the *c* axis perpendicular to the surface which was observed in the thin layer of 123 remaining on the surface of the substrates with a high open porosity, one may speculate that this orientation may result from the deposition of the 123 nuclei flat on the surface when the liquid phase



← 123

← 211

Figure 4. Section of a 123 film obtained after a diffusion reaction of 20h at 980°C on a substrate sintered 90h at 1150°C.

where they were growing has been leached out as a result of its infiltration into the open porosity.

4. Conclusion

Dense films of 123 phase have been produced by solid/liquid diffusion on 211 substrates. The microstructure of the superconducting layer was found to be dependent on the microstructure of the substrates. The results suggest that 123 nucleates and grows on the 211 solid surface when this material is dense enough to avoid the infiltration of the liquid. A columnar morphology of the film is obtained due to the alignment of the 123 platelets perpendicular to the surface.

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References

1. S. Jin and J.E. Graebner, *Mater. Sci. Eng.B* 7 (1991), 243.
2. M. Murakami, *Supercond. Sci. Technol.* 5 (1992), 185.
3. S. Jin, G.W. Kammlott, T.H. Tiefel, T.T. Kodas, T.L. Ward and D.M. Kroeger, *Physica C* 181 (1991), 57.
4. M.A. Rodriguez, B.-J. Chen and R.L. Snyder, *Physica C* 195 (1992) 185.
5. B.-J. Chen, M.A. Rodriguez, S.T. Mixture and R.L. Snyder, *Physica C* 198 (1992), 118.
6. K. Tachikawa, N. Sadakata, M. Sugimoto and O. Kohno, *Jpn. J. Appl. Phys.* 27 (1988), L1501.
7. N. Sadakata, M. Sugimoto, O. Kohno and K. Tachikawa, *IEEE Trans. Mag.* 25 (1989), 2180.
8. P.A. Freeman, N. Özkan, P.D. Honneyball and B.A. Glowacki, *Supercond. Sci. Technol.* 4 (1991), S358.
9. P.A. Freeman and B.A. Glowacki, *High Temperature Superconductors*, P. Vincenzini (ed.), Elsevier Science Publishers B.V., 1991.
10. K. Lee and G. Park, *Appl. Phys. Lett.* 60 (1992), 651.
11. J.D. Verhoeven, E.D. Gibson, L.S. Chumbley, R.W. McCallum and H.H. Baker, *J. Appl. Phys.* 64 (1988), 761.