Journal of the European Ceramic Society **8** (1991) 41–45

Highly Textured Thick Layers of YBCO Superconductor

F. Guérin*

Ceramics Department, Central Research Laboratory, Thomson-CSF, Domaine de Corbeville, 91404 Orsay Cedex, France

F. Lainée† & J. Massol

Materials Research Department, Ecole des Mines de Paris, 9100 Evry, France

(Received 15 December 1990; revised version received 1 February 1991; accepted 25 February 1991)

Abstract

A screen-printing technique has been used to obtain thick layers of YBCO on a ceramic substrate. By using a metallic buffer layer and a melt-growth technique in a localized temperature gradient highly textured layers of YBCO have been obtained, with the a–b plane parallel to the layer.

Mit einem Siebdruckverfahren wurden dicke YBCO-Schichten auf einem keramischen Substrat hergestellt. In Verbindung mit einer metallischen Zwischenschicht und einem Kristallwachstum aus der Schmelze mittels eines kontrollierten Temperaturgradienten konnten YBCO-Schichten mit ausgeprägter Textur hergestellt werden, bei denen die a–b-Ebene parallel zur Schicht liegt.

On a mis en œuvre une technique de sérigraphie afin d'obtenir des couches épaisses de YBCO sur un substrat céramique. Par utilisation d'une couche tampon métallique et d'une technique de croissance-fusion dans un gradient de température localisé, on a obtenu des couches de YBCO fortement orientées, dont le plan a–b était parallèle à la couche.

1 Introduction

Since the discovery of high-temperature superconducting oxides a few years ago all kinds of shaping techniques have been employed to prepare them.

The screen-printing technique is commonly used in electronic industries for making thick films for interconnection or passive components (capacitors, inductors, etc.). In such applications superconductors, when compared with copper or gold, would have the advantage of reduced losses.

This motivated the previous studies of screen-printing techniques applied to oxide superconductors.[1–4] Those studies clearly demonstrated the two main limitations of screen-printing high T_c superconducting thick films:

(1) The chemical interaction with most substrates in the sintering temperature range.
(2) The very low critical current density (J_c) of films sintered below their decomposition temperature (J_c in the range of 100 Acm^{-2} at 77K).

This low J_c problem is also present, although to a smaller extent, in bulk samples of superconducting oxides. In 1988 Jin *et al.*[5] proposed a melt-textured growth technique (MTG) to produce bulk YBCO samples having a microstructure consisting of highly aligned long grains and exhibiting high J_c values ($>10^4$ Acm^{-2} at 77K). MTG was then applied to thick superconducting films so as to produce textured films with improved electrical properties.[6–9]

A method is described here for preparing thick films of YBCO which is a step towards solving the two main problems presented. The method consists in melt-texturing a YBCO thick film deposited on an alumina substrate. A metallic buffer layer protects the film from degradation occurring through a reaction with the substrate. The sintering of films is conducted in a localized temperature gradient, leading to a very high texture of the film.

* Present address: Thomson Broadcast, 17, rue du Petit Albi, BP 8244, 95801 Cergy Saint-Christophe Cedex, France.
† To whom all correspondence should be addressed.

2 Experimental procedure

A YBCO powder provided by Rhône-Poulenc (France) was mixed with terpineol in appropriate quantities in an agate mortar so as to produce a screen-printing paste.

This paste was either screen-printed or deposited with a brush on three kinds of substrates:

—Substrate I: Tape-casted sintered alumina.
—Substrate II: Substrate I covered with a screen-printed and sintered silver layer 10 μm thick.
—Substrate III: Same as substrate II with silver replaced by 70% silver–30% palladium.

The screen-printed YBCO tracks were deposited through a 325 mesh stainless screen. They were 20 μm thick before sintering and about 15 μm thick after sintering. Tracks deposited with the brush were 70 to 80 μm thick after sintering. The tracks were sintered according to one of the two following methods:

(1) Homogeneous temperature furnace: According to the cycle of Fig. 1. T_M was kept below the decomposition temperature of YBCO ($\approx$1015°C in air), varying between 910°C and 950°C; t_P was varied between 18 min and 16 h.
(2) Temperature gradient furnace: As shown in Figs 2 and 3 this furnace, working in air, consisted of two parts. In the lower part the substrate was homogeneously heated at about 800–850°C. The upper part consisted of a heating resistance. It created in the layer a maximum temperature T_M which was fixed between 1050 and 1150°C, above the decomposition temperature of YBCO. It also created a temperature gradient of approximately 15°C mm^{-1} in the temperature range (800°C to T_M). The heating rod could move at a speed V, so that the decomposed zone of YBCO could be moved along the sample. A similar furnace was used by Miaoulis *et al.*[10] for texturing YBCO and BSCCO thick films, but in their work it failed to texture YBCO films.

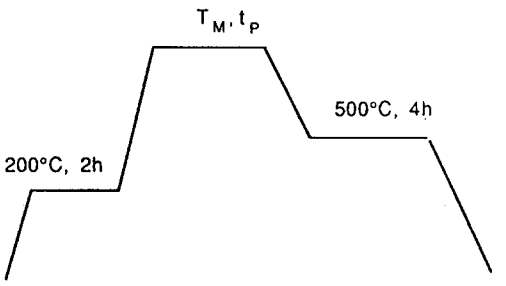

Fig. 1. Sintering cycle of samples. Heating and cooling rates: 1°C min^{-1}; atmosphere: flowing oxygen.

In both conditions after sintering the samples were annealed in flowing oxygen at 500°C for 4 h.

3 Results

The results for a series of seven samples are presented in Table 1.

Experiments conducted on those samples were used to prove the influence of three factors on the quality of superconducting YBCO screen-printed films.

3.1 Influence of the substrate

From Fig. 4 it is clear that silver used as a buffer layer is useful to prevent reaction between alumina and

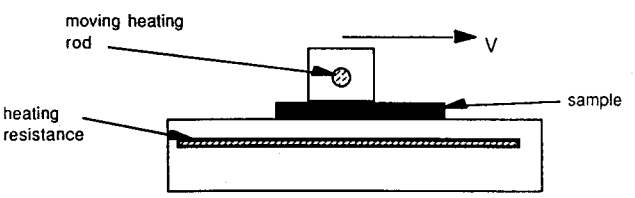

Fig. 2. Principle of the gradient furnace.

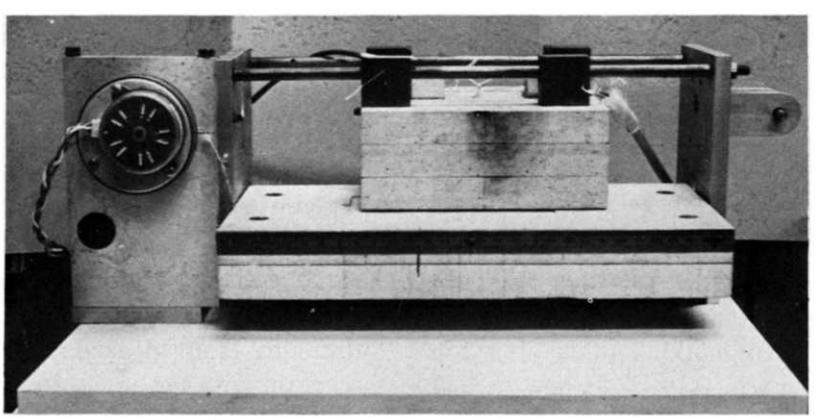

Fig. 3. Photograph of the temperature gradient furnace.

Table 1.

Sample	*Thickness* (μm)	*Substrate*	*Sintering conditions*
A	10	I	(1) $T_M = 910°C$, $t_P = 16\,h$
B	10	II	(1) $T_M = 910°C$, $t_P = 16\,h$
C	10	III	(1) $T_M = 925°C$, $t_P = 2\,h$
D	80	III	(1) $T_M = 925°C$, $t_P = 2\,h$
E	80	I	(2) $V = 30\,mm/h$
F	80	III	(2) $V = 30\,mm/h$
G	80	III	(2) $V = 8\,mm/h$

YBCO film, resulting in a narrow superconducting transition ($\Delta T < 2\,K$, $T_{c(R=0)} \approx 91\,K$).

SEM observation also shows a larger grain size in sample B when compared with sample A. This is probably due to the enhanced diffusion of matter assisted by silver, as T_M is close to the melting point of silver. Sample A also shows many more cracks than sample B. This is probably due to differential dilatation. As $\alpha_{alumina} < \alpha_{YBCO} < \alpha_{silver}$, the alumina substrate will create traction strains in YBCO films during cooling, while a silver buffer layer will create compression strains.

Thus an alumina substrate is likely to open cracks in the YBCO layer while a metallic layer ($\alpha > \alpha_{YBCO}$) should not.

3.2 Influence of the YBCO layer thickness

YBCO layer thickness is also a relevant parameter to control film quality. Figure 5 shows this through resistivity measurements of films deposited on Ag/Pd buffer layer. In agreement with the results of Ref. 9 there is a degradation of superconducting properties due to a reaction between Pd and YBCO. For thin layers this results in a suppression of superconductivity above 60 K, while $T_{c(R=0)} = 88\,K$ for an 80 μm thick film.

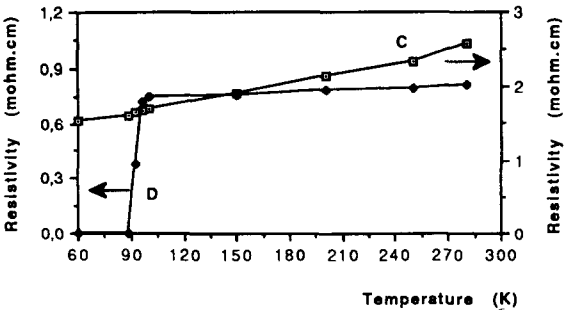

Fig. 5. Influence of track thickness resistivity versus temperature. Sample C, 10 μm thick; sample D, 80 μm thick.

3.3 Influence of the sintering conditions for texturing

However, whatever substrate is used, YBCO films sintered according to conditions 1 (Table 1) prove not to have any texture. This is completely different from what is obtained with the temperature gradient melt and growth method.

Before addressing the texturing properties of the methods a series of remarks must be made dealing with phase purity of the MTG tracks:

On the X-ray spectrum of sample E second phase peaks corresponding to Y_2BaCuO_5, $BaCuO_2$, CuO, Cu_2O can be detected. These phases appear above 1015°C, when YBCO decomposes. During cooling the high reactivity of alumina with the Ba-rich liquid phase is likely to prevent complete recrystallization.

The influence of the substrate on phase purity of MTG tracks can be seen in Fig. 6 which shows the much smaller amount of second phases present in sample F (having a diffusion barrier of Ag–Pd) when compared with sample E (without any diffusion barrier), although the sintering conditions were the same.

The effect of those second phases is not obvious: on the one hand a high proportion of non-superconducting second phases means a low proportion of superconducting phase and a low connectivity of superconducting electric paths. On the other hand a correct distribution of second phase

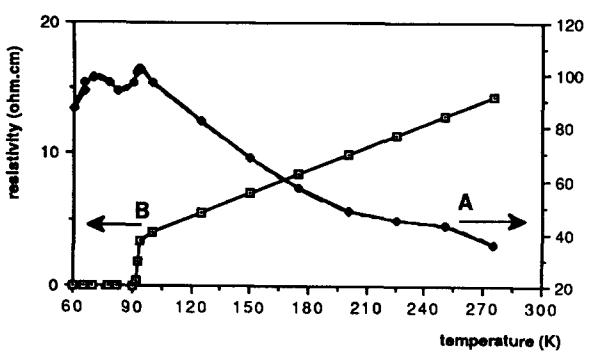

Fig. 4. Influence of the substrate resistivity versus temperature. A, Alumina substrate; B, silver substrate.

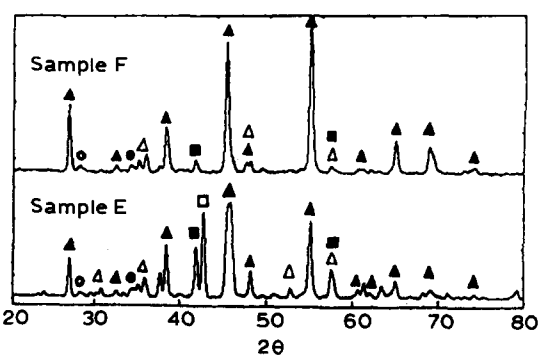

Fig. 6. X-Ray diagram for samples E and F. ▲, YBCO; △, Y_2BaCuO_5; ●, $BaCuO_2$; ○, $BaCO_3$; ■, CuO; □, Cu_2O.

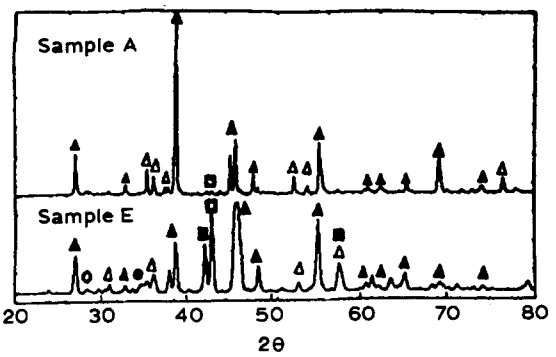

Fig. 7. X-Ray diagram for samples A and E. ▲, YBCO; △, Y_2BaCuO_5; ●, $BaCuO_2$; ○, $BaCO_3$; ■, CuO; □, Cu_2O.

among superconducting grains can be useful as a collection of flux pinning centres.

$BaCO_3$, present in most samples after sintering, was not detected in the starting material. It probably appeared through a reaction with air at high temperature. Better control of the sintering atmosphere will avoid the formation of this second phase.

The texturing properties can now be considered. From Fig. 7 it is clear that the growth method itself has a strong texturing power: indeed 001 peaks are strongly enhanced when the X-ray spectrum of sample E is compared with the one of sample A. Sample G, prepared at a gradient scanning speed eight times lower than sample F, shows almost complete texturing with the *c*-axis of grains perpendicular to the substrate (Fig. 8), thereby proving the importance of a low recrystallization speed.

The texturing of the films is the result of a drastic change of microstructure, as can be seen from Figs 9, 10 and 11.

Through type 1 sintering conditions films consist of an assembly of small ($\approx 10\,\mu m$) platelet-like grains, showing no coherent orientation between neighbouring grains. Through type 2 sintering films consist of large (several hundreds of microns) platelet-like grains extending along the surface. Several platelets may grow in the thickness of the sample, keeping parallel to one another. In some

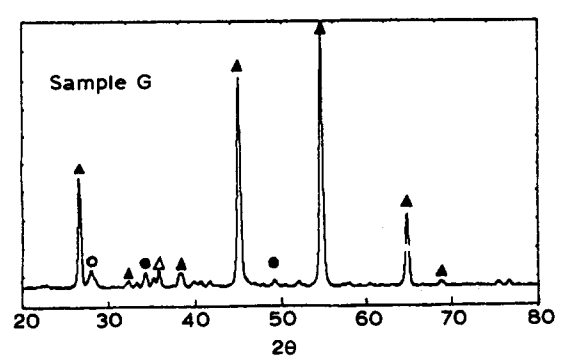

Fig. 8. X-Ray diagram for sample G. ▲, YBCO; △, Y_2BaCuO_5; ●, $BaCuO_2$; ○, $BaCO_3$.

Fig. 9. Microstructure of sample A.

regions unreacted CuO films cover the surface of the sample. Two other microstructural features are obvious on the samples:

—Large holes ($> 50\,\mu m$) are present in the grains. EDX shows a copper-rich phase, probably CuO, in the bottom of those holes. Those holes may appear on cooling. Indeed, the platelets grow in an abundant liquid phase. If in some areas of the recrystallizing film a liquid zone is surrounded by recrystallized matter, the volume change occurring when the liquid phase turns solid will leave large pores in the film.

—A network of cracks crossing the grains, uniformly distributed on the surface of the samples. Those cracks may also be accounted for by the volume change at solidification, since the buffer layer does not experience any significant dilatation when the volume loss takes place at solidification. Those cracks may

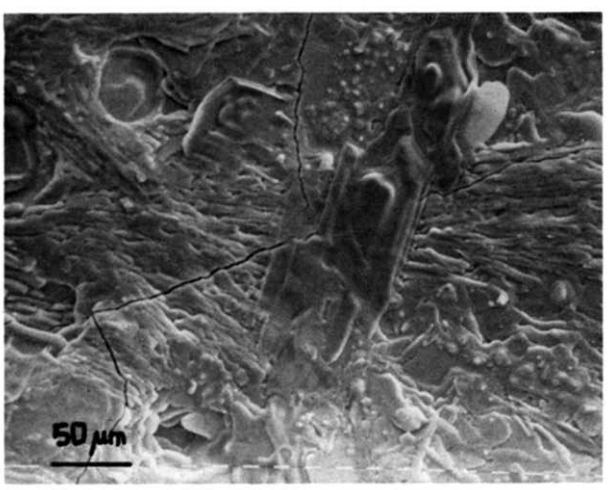

Fig. 10. Microstructure of samples F or G.

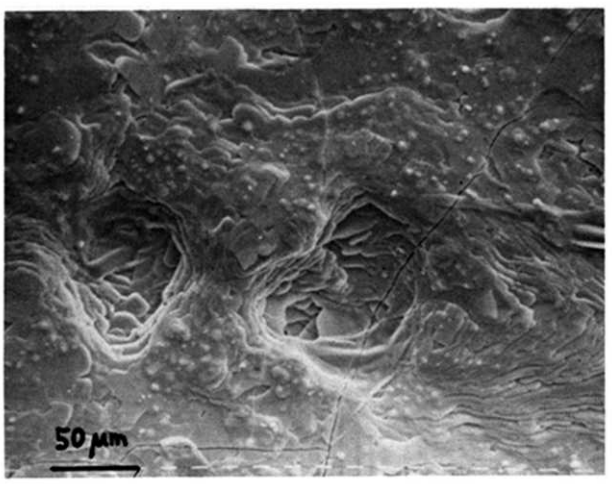

Fig. 11. Microstructure of samples F or G.

also be caused by the thermal strain induced by a too-rapid cooling. It must be noted that these tracks have not, in any way, been optimized as concerns crack formation. Further work is in progress to study this point.

The resistivity/temperature curves of samples F and G are displayed in Fig. 12. For both, $T_{c\,onset}$ is 92 K. $T_{c(R=0)}$ is lower than 60 K for sample F, and is 75 K for sample G. This suggests that the superconducting phase is much better connected in the volume of the sample when enough time is left for the recrystallization process. Further work concerning the cracks should also help to improve those electrical results.

4 Conclusion

In this study it has been proven that silver or silver–palladium buffer layers can be used to obtain YBCO thick films having $T_{c(R=0)}$ as high as 88 K.

A local temperature gradient inducing directional melting and recrystallization can provide almost complete textured films on those buffer layers. The films thus produced have the *c*-axis perpendicular to the substrate.

These preliminary results are quite encouraging steps in the path leading to high-J_c YBCO tracks on alumina substrates.

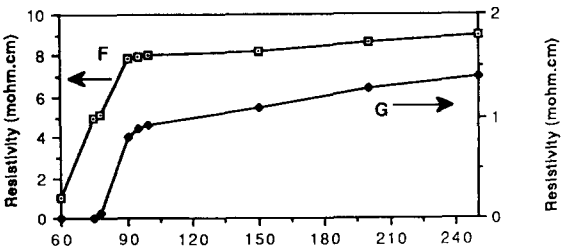

Fig. 12. Influence of the crystallization speed resistivity versus temperature. Sample F, $V = 30\,\text{mm h}^{-1}$; sample G, $V = 8\,\text{mm h}^{-1}$.

Acknowledgements

The authors wish to thank R. Kormann from Thomson-CSF for numerous useful discussions and advice. The authors also thank M. Durand from Ecole des Mines for conducting the X-ray experiments.

References

1. Baudry, H., Réalisation de films supraconducteurs par sérigraphie. In *Proceedings of the 1st SEE Conference*, Caen, France, 13–14 September 1988.
2. Kokkomaki, T., *et al.*, Screen-printed superconducting YBCO thick films on various substrates. *Active and Passive Components*, **13** (1989) 197–209.
3. Tabuchi, J., *et al.*, Fabrication of screen-printed high-T_c superconducting oxide thick films on various substrates. *J. Ceramics Soc. Inter. Ed.*, **16** (1988) 441–4.
4. Sachi, M., *et al.*, High-T_c superconductivity in YBCO screen-printed films. *Appl. Phys. Lett.*, **53** (1988) 1110–12.
5. Jin, S., *et al.*, High critical currents in YBCO superconductors. *Appl. Phys. Lett.*, **52** (1988) 2074–6.
6. Abell, J. S., *et al.*, Textured superconducting thick films of YBCO. In *Proceedings of the 1st ECRS Conference*, Maastricht, June 1989.
7. Matsuoka, Y., High-T_c screen-printed YBCO films prepared by a liquid-phase processing method. *J. Phys. D, Appl. Phys.*, **22** (1989) 1935–7.
8. Button, T. W., *et al.*, The processing and properties of high-T_c thick films. In *Proceedings of ASC Snowmass*, 1990.
9. Taffin, A., *et al.*, Ocuches épaisses supraconductrices de YBaCuO préparées par sérigraphie sur des substrats polycristallins. In *Proceedings of the 2nd SEE Conference*, Caen, France, 6–7 November 1990.
10. Miaoulis, I. N., *et al.*, Zone-melting processing of thick high-T_c superconducting films. *J. Phys. D, Appl. Phys.*, **22** (1989) 864–7.