Annealing of electrophoretic $\text{YBa}_2\text{Cu}_3\text{O}_7$ coatings on polycrystalline substrates by zonal laser fusion

E. TEJADA-ROSALES¹, S. ONDOÑO-CASTILLO¹, C. DÍEZ², G. DE LA FUENTE², N. CASAÑ-PASTOR¹

¹Instituto de Ciencia de Materiales de Barcelona, Campus UAB, 08193 Bellaterra, Barcelona.

²Instituto de Ciencia de Materiales de Aragón, (CSIC- Universidad de Zaragoza) 50015 Zaragoza

Obtaining coatings on metallic substrates of irregular geometries is not easy by traditional methods. In those cases electrochemical methods show important advantages and have been used successfully. To date only silver has shown to be inert with respect to superconducting cuprates, although progress has been made in the development of intermediate buffer layers. However, in the particular case of $\text{YBa}_2\text{Cu}_3\text{O}_7$, annealing above the cuprate superconducting melting point to attempt densification or texturing is hard on silver because of the lower melting point of the metal. Focalized heating of superconducting oxides over metallic substrates, using LASER techniques on controlled geometries, allows densification of coatings. The Laser processed sample may be amorphous but the crystallinity is easily recovered, as well as the optimal oxygen content for the oxide, but the preferential orientation induced by the electrophoretic deposition is lost upon the recrystallization process occurring over polycrystalline substrates.

Keywords: superconductors, electrochemistry, electrophoresis, annealing, LFZ

Tratamiento de depósitos electroforéticos de $\text{YBa}_2\text{Cu}_3\text{O}_7$ sobre sustratos policristalinos mediante fusión zonal por láser

La realización de depósitos de óxidos superconductores sobre sustratos metálicos de geometría compleja y en general policristalinos está prácticamente basada en métodos electroforéticos o electroquímicos que permiten la utilización de un campo eléctrico de geometría definida para inducir el movimiento de partículas de óxido o de precursores de éste, hacia el electrodo elegido. Dichos métodos son fundamentales cuando el sustrato es metálico o puede hacerse metálico con facilidad. Hasta el presente tan sólo la plata ha mostrado ser lo suficientemente inerte para permitir recocidos posteriores, aunque se está progresando en el desarrollo de capas "buffer". Sin embargo, cuando el óxido depositado es $\text{YBa}_2\text{Cu}_3\text{O}_7$, el proceso de recocido posterior no permite la obtención de textura sobre Ag mediante métodos térmicos dado el inferior punto de fusión de este metal. El presente trabajo presenta un estudio de fusión zonal por láser que permite recocer el óxido sin fundir el sustrato metálico de plata. El control de las distintas variables permite llegar a una solución en la que se puede preservar la naturaleza superconductora del depósito y su densificación. Ello requiere un tratamiento térmico posterior que recupera la cristalinidad y el contenido óptimo de oxígeno. Sin embargo, el tratamiento disminuye la orientación preferencial de las partículas de $\text{YBa}_2\text{Cu}_3\text{O}_7$ que se obtiene mediante la deposición electroforética.

Palabras clave: superconductores, electroquímica, electroforesis, recocido, LFZ

1. INTRODUCTION

A crucial step that will decide the extent in which high T_c superconductors will be used in technical applications is related with the ability of supporting them on substrates with the mechanical strength that they do not have as ceramic materials. This is specially true when the application needs low weight, resistant materials with optimal physical properties. To date, the optimal values of critical currents, I_c , have been achieved either in bulk-textured dense ceramic materials, (1) while large values of J_c have been obtained only for thin layers deposited by methods such as sputtering, CVD, etc (1). In the first case, texturing to the desired orientation of highly anisotropic particles, is possible by inducing melting along with thermal gradients on the pure bulk pellet at high temperatures, which will allow to recrystallize the oxide in the optimal orientation. In the second, epitaxial growth on oriented substrates allows superconducting oxide crystals to grow in the appropriate direction. Those coatings, however, are very thin and do not

support large absolute currents. The intermediate stage, large I_c , thick coatings onto substrates that may offer the mechanical strength that the oxide needs, is not comparatively so successful. Thick coatings do not have the advantage of epitaxial growth, and no success has been achieved on texturing them by melting methods.

In that sense, electrophoretic deposition of superconducting oxides is among the simplest and most inexpensive methods available to obtain good-quality, homogeneous, even-thickness coatings of superconducting oxides on polycrystalline substrates of any size and geometry. Previous results from other laboratories and our own (2-9) using metallic silver substrates show good quality coatings after annealing, with I_c and J_c values measured by transport measurements reaching 3 A and 6000 A/cm² respectively for $\text{YBa}_2\text{Cu}_3\text{O}_7$, without any attempted melt-texturing procedure. The substrate used in this method needs to be a metal or a metallized material. Among all metals tested, only silver has

shown to be inert with respect to the copper oxides. (7-9) In addition, in those coatings, silver is found to diffuse throughout the oxide grains. This diffusion takes place in larger extent in the region closer to the substrate and explains the good mechanical properties of coatings sintered at very low temperatures (920°C). (7-10). It may also explain, in addition, the good J_c values obtained for polycrystalline materials. Taking into account that silver is among the few, if not the only, substrate that does not react chemically with the oxide, it may be considered the substrate of choice when the later needs to be metallic. However, the relatively low melting point of silver difficults any succesful melt-texturing process for the oxide since most of the superconducting oxides melt at larger temperatures. The intensive effort performed on melt texturing high T_c superconductors over many types of substrates is enormous and cannot be described here, but in no case it has been successful when the oxide was deposited on a substrate. [See for example (11)]. Alternative processing resources need to be investigated that may lead to the desired microstructure for the superconducting oxide.

In particular, the electrophoresis process offers a certain degree of preferential orientation, not yet texturing, that derives from the existence of the same electric field that moves the particles towards the electrode. Preferential orientation has been observed for electrophoretic coatings of anisotropic $\text{YBa}_2\text{Cu}_3\text{O}_7$ particles (9,10,12) as reported by several authors. Such orientation is highly dependent on electric field geometry and electrode disposition within the electric field, as well as on any additional force involved (gravitational force or stirring for example) (10,12) and can be explained assuming that the two-dimensional oxide particle behaves as a dipole within the applied electric field. Once the electrophoretic coating is obtained over a certain substrate, any annealing performed below the silver melting point preserves the orientation of oxide particles, but does not allow recrystallization to induce texture.

In order to raise the temperature to attempt texturing, alternative inert substrates with higher melting points need to be found. In that sense, Au, Ag-Pd alloys have been used as substrates (10). However, when palladium is present we have observed de composition of the superconductor, similar to that described for platinum. When gold is used as substrate, no chemical reaction seems to occur, but classical melt texturing methods yield to a worsening on the previous preferential orientation. That lost orientation suggests that the substrate may be acting as nucleation center during the melting and recrystallization process of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with the standard gradients that can be used in tubular furnaces (10).

Other attempts to apply melt-texturing methods are based on the well known fact that the $\text{YBa}_2\text{Cu}_3\text{O}_7$ oxide peritectic point is decreased by lowering the partial pressure of oxygen (13). However, according to our own experiments, this effect is not sufficient when silver is used as substrate, (10) probably due to the fact that silver-copper alloys may be formed in the process, because of copper reduction in absence of oxygen.

An alternative method, followed in this work, is to apply a temperature gradient that could allow heating the oxide without raising the temperature of silver and of the interface substrate-oxide, too close to its melting point, preventing in addition the formation of copper-silver alloys. This gradient is difficult to obtain in the standard tubular furnaces for obvious reasons, and requires a fast responding heating element used in an arrangement that could allow silver dissipate heat and to remain cold enough during the processing. Therefore the

gradient induced would indeed be larger than the usual one required for texturing. This approach would not eliminate the existence of a solid phase on which recrystallization could occur but could modify the direction of solidification. A fast-responding heating system is indeed a focussed LASER used in a set of conditions that may allow efficient heat dissipation of the metal acting as substrate.

This paper describes the results obtained along this line of work, using CO_2 and Nd-doped Yttrium Aluminum Garnet LASERS under pulsed and continuous wave operation modes, on coatings obtained by electrophoretic methods on planar vertical cells. In the range of energies applied by the LASER system, and its application setup, which may allow different degrees of dissipation of heat during the treatment, there are many variables involved. The results shown represent just a preliminary study of what is possible to obtain by combining electrochemical methods of deposition and localized thermal annealing or selective area zone melting with LASER techniques.

2. EXPERIMENTAL PROCEDURE

$\text{YBa}_2\text{Cu}_3\text{O}_7$ was used as purchased from SSC, Inc and its phase composition confirmed by powder Xray diffraction. Suspensions of the oxide in isobutyl-methyl-ketone were prepared in previously optimized concentrations. (9, 10, 12) 2% oxide by weight suspensions were prepared, using 0.05 % I_2 as additive to improve charging of the particles. Under these conditions the particles get charged positively and migrate towards the negative electrode. Electrophoretic cells were set up using a Teflon™ holder that kept two sheets, one being the working silver electrode and the other one a counter-electrode stainless steel plate, at a fixed parallel geometry and constant distance from each other. Electric potentials ranging from 300 to 500 V were applied between the two electrodes in the suspension. Cylindrical objects were also deposited by this method, but in that case, Laser treatments induced a considerable softening of Ag during heating. Distance between plates acting as electrodes were 1.2 cm. Deposition was performed in vertical geometries using Teflon™ holders and were complete within the first 30 sec to 2 minutes of the start of the experiment. This fast speed implied that the thickness could only be controlled by modifying the applied potential, rather than by controlling deposition time. The power source used for electrophoretic deposition was a Labconco (0-1000V, 0-0.5A), under potentiostatic conditions. Usual observed currents were in the 1 mA regime. All experiments were carried out inside the fume hood, given the large volatility of the ketone. Oxide particles are deposited in the negative electrode showing that they acquire a positive charge, as studied previously. Final deposits were dried in air and treated thermally at 920°C to remove excess solvent and improve grain connectivity prior to the Laser treatment. Thermally untreated samples were easily removed from the substrate by the laser beam used as the next stage in the process.

The above coatings were subsequently processed using two LASER heating techniques described previously (14,15). On the one hand, Laser Induced Zone Melting was applied on a XY- coordinate axis table on which the CO_2 LASER (Laser Quanta, $\lambda = 10.6 \mu\text{m}$) was programmed to incide, adjusting the Laser beam focusing area to a thin long line (aprox. $0.5 \times 22 \text{ mm}^2$ in area) by using a specially designed parabolic

mirror. A wide range of Laser power conditions was studied, although a power level of 125 Watts was found convenient when focused onto a 11 mm² strip using a CO₂ Laser.

In addition, a Q-switched Nd:YAG Laser (Baasel Lasertech, Germany, $\lambda = 1064$ nm) fitted with a galvanometric mirror beam maneuvering system and operating in cw mode, was focused onto a point, aprox. 490 μm^2 in area, with a power range of 4 to 8 Watts. This focused Laser beam was scanned through a predetermined area of the sample whose geometry was configured on a CAD-controlled computer system. The geometric figure was completely filled by the Laser point by displacing the coating describing straight lines arranged in a parallel fashion. Scanning speeds of 250 to 400 mm.s⁻¹ were studied with the Nd:YAG galvanometric system.

For the XY stage CO₂ system the transverse speeds studied were exclusively limited to 36 to 72 mm/hr. Insulating ceramic or metallic supports for the Ag-YBa₂Cu₃O₇ assembly were used to allow different heat dissipation conditions. The authors consider that each particular set of LASER and optics is very unique and an optimal set of conditions needed to be found in each case. The results derived from both systems are quite different and are described in the following section. Thermal annealing in standard furnaces under oxygen atmosphere was found to be necessary after the LASER processing, in order to recover, when possible, the oxide superconducting properties, and its crystallinity. In the latter treatment, thermal annealing was performed initially at 920°C, followed by an oxygen uptake at 450°C during 12 hours. Transport properties were measured using the 4-contact method at liquid nitrogen temperatures with a 1 $\mu\text{V}/\text{cm}$ criteria. Xray diffraction and Scanning Microscopy studies were also performed before and after the thermal annealing procedure.

3. RESULTS AND DISCUSSION

Samples prepared in optimal electrophoresis conditions as reported previously (9,10,12) were treated in a set of conditions particular for each LASER system, geometry and optics. Annealing at 920°C was needed prior to LASER treatment to give each sample good mechanical properties that proved to be essential on the first thermal shock that suffers under the LASER beam. Thus, deposits that had not been thermally annealed before hand tended to be physically removed from the substrate by the focalized heating.

CO₂-laser processing of the superconducting oxide/Ag in contact with either ceramic insulating supports or metallic

Figure 1: a) b) c) Optical Microscopy of Electrophoretic $\text{YBa}_2\text{Cu}_3\text{O}_7$ Coatings a) untreated (x20) and b) y c) treated with laser CO₂. (b) (x50) c) (x200); d) SEM of $\text{YBa}_2\text{Cu}_3\text{O}_7$ coatings without CO₂ LASER treatment and e) with CO₂ LASER treatment

supports did not allow good heat dissipation. This fact derives from the oxide's poor heat conductivity, and the nature of the CO₂ laser radiation impressed in a slow transverse speed over the oxide. Such middle infrared radiation is absorbed by the oxide at the outer layers and penetrating only to a limited depth with the coating. (Most of the oxide is therefore heated by other mechanisms different from laser direct irradiation). Although that was considered originally an advantage that could allow thermal annealing of the oxide without melting the silver substrate, the experiments showed that it did induced a more profound melting in the borders of the Ag-YBa₂Cu₃O_{7-d} sheets where dissipation occurs mainly in only one direction. In samples treated with CO₂, therefore, transport measurements refer to a sample that is not homogeneous and therefore are minimum limits to what can really be achieved. The final sheets were bent with respect to the original, and showed macroscopic and microscopic heterogeneities. Figure 1 shows a comparison of various zones in the same treated deposit, after annealing. X ray diffraction patterns obtained on this coating after LASER processing show the existence of green phase, Y_2BaCuO_5 , and poor crystallinity. (See Figure 3) However, after thermal annealing at 920°C and oxygen treatment at 450°C, the pure superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ phase is found, and transport measurements can be performed.

YAG pulsed laser processing in *cw* mode allowed a much more efficient heat dissipation probably because of the combination of a much shorter wave length and the larger scanning speed over the coatings. Processing with this particular set up yielded superconducting sheets with a very

Figure 2. Optical microscopy of $\text{YBa}_2\text{Cu}_3\text{O}_7$ coatings on Ag a) no LASER treatment b) LFZ. (YAG), $\times 20$

uniform microstructure which exhibited a powder diffraction pattern typical of an amorphous phase. Annealing in tubular furnaces at 920°C and later at 450°C in oxygen allows recrystallization and recovery of the superconducting properties of the material, with an Xray powder diffraction pattern corresponding to pure orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$. No decomposition into green phase is observed. Figure 1d,e shows an electron microscopic image of the coating after annealing.

Optimal I_c values, 3 A , (J_c for the same sample 700 A/cm^2) resemble those of the precursor thick coatings in the best conditions (300 A/cm^2 for thick deposits, 6000 A/cm^2 for thin) (see Figure 5). Taking into account that a densification has occurred, that involves at least a two-fold increase in critical current densities. Thus, the J_c values obtained are larger than for any other electrophoretic $\text{YBa}_2\text{Cu}_3\text{O}_7$ deposit on polycrystalline Ag substrates.

As observed previously for other deposits obtained by electrodeposition and electrophoresis, silver diffuses through the grain boundaries, yielding a deposit with larger mechanical resistance than bulk materials. Silver content in the deposit decreases as the distance from the substrate increases. Apparently this diffusion does not prevent superconducting currents going through the deposit.

Figure 3. Comparison of X ray powder diffractograms on CO_2 LASER treated samples, before and after a further thermal treatment in a conventional oven under oxygen.

Figure 4. Comparison of X ray diffractograms of treated and untreated deposits (YAG)

Figure 5. I_c for treated and untreated coating using YAG LASER

According to Xray diffraction the crystallinity of the deposit may be recovered but the intensity ratio among diffraction peaks shows that the orientation of crystals may have varied considerably with respect to the deposit obtained by electrophoresis. In other words, the preferential orientation that is observed for electrophoretic deposits (9, 10,12) with the oxide ab plane parallel to the substrate, the ideal situation, is lost upon thermal processing and recrystallization onto the silver polycrystalline substrate. (See Figure 4). Densification

derived by the Laser processing is, however, remarkable and can be observed macroscopically. Therefore, the obtention of similar critical current values before and after LASER treatments maybe considered a balance among orientation and grain connectivity.

4. CONCLUSIONS

As a summary, the treatment with LASER focalized heating allows a great densification and sintering of the particles deposited by alternative methods, in the present case electrophoresis, when using low melting point substrates such as silver. However, the LASER process itself suffers from the same problems generally found when a recrystallization from a melt occurs over a substrate. The substrate seems to induce an orientation that goes against the preferred orientation for optimal conduction, as expected from a process controlled largely by nucleation kinetics. Further improvement may be achieved by a similar process that do not reach recrystallization temperatures.

LASER zonal treatment, with either CO_2 or Nd-YAG LASERS, of $\text{YBa}_2\text{Cu}_3\text{O}_x$ coatings obtained by electrophoretic methods over silver is adequate for sintering and densification of the oxide without melting the underlying silver substrate. That, however, needs of a previous thermal treatment and a posterior annealing that will recover the oxide crystallinity, optimal oxygen content and physical properties.

ACKNOWLEDGEMENTS

The authors want to thank the Spanish Ministry of Culture (former Science and Education) for financing through grants CICYT MAT96-1057-c02-01, PB98-0491 and graduate fellowships, and REE for the contract CSIC-REE on 1997-1998.

REFERENCES

1. "Chemistry of Superconductor Materials" Ed. T.A. Vanderah, Noyes Pub. 1992
2. R.N.Battacharya, P.A.Parrilla, R.Noufi. "YBaCuO and TlBaCaCuO Thin Films via an Electrodeposition Process" J. Electrochem. Soc. **139**, 67 (1992).
3. R.N.Battacharya, P.A.Parilla, A. Mason, L.L. Roybal, R.K.Ahrendiel, R. Noufi, R.P. Hellmer, J.F. Kwak, D.S. Ginley. "YBaCuO Thin Films via an Electrodeposition Process" J. Mater. Res. **6** (7), 1389 (1991).
4. A. Weston, S. Lavani, N. Ali. "Synthesis of Y-Ba-Cu-O Films by an Electrodeposition Technique" J. Mat. Sci. **2**, 129 (1991).
5. J.M. Rosamilia, B. Miller, "Additive Enhanced Nonaqueous Electrodeposition of Silver on $\text{Ba}_2\text{YCu}_3\text{O}_7$ " J. Mater. Res. **5**, 1612 (1990).
6. P. Slezak, A. Wieckowxki. "Aqueous Electrochemical Synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_x$ -Superconductors" J. Electrochem. Soc. **138** (4), 1038 (1991).
7. N. Casañ-Pastor, P. Gómez-Romero, A. Fuertes, M. Brossa. "YBa₂Cu₃O_{7-y} Wires by Electrodeposition of Metallic Elements and by Electrophoresis", Sol. State Ionics. **66**, 241 (1993).
8. S. Ondoño-Castillo, F. Pérez, A. Fuertes, P. Gómez-Romero, N. Casañ-Pastor. "Superconducting YBa₂Cu₃O_{7-δ} Wires by Simultaneous Electrodeposition of Y, Ba and Cu in Presence of Cyanide". Chemistry of Materials, **7**, 771 (1995).
9. S. Ondoño-Castillo, N. Casañ-Pastor. "Deposition of YBa₂Cu₃O_{7-δ} over Metallic Wires by Electrophoresis of Suspensions in Isobutylmethylketone. Influence of Electric Field, Thermal and Mechanical Treatments" Physica C **268**, 317 (1996).
10. S. Ondoño, "Obtención de Artículos Superconductores por Electrodeposición y Electroforesis" Doctoral Dissertation, UAB, Barcelona, 1996
11. N. Zaffar, J.J. Wells, A. Crossley, J.L. MacManus, "Texturing of Thick Film ReBCO on Metallic Substrates by Isothermal Melt Processing" Applied Superconductivity 1997, H. Rogalla and D.H. A. Blank eds. I.O.P. n. 158, p. 877 (1997)
12. C. Zinck, S. Ondoño, N. Casañ-Pastor, unpublished results.
13. J. L. MacManus-Driscoll, J.C. Brauman, R. Beyers, "Phase Equilibria in the Y-Ba-Cu-O System and Melt-processing of the Ag Clad YBa₂Cu₃O₇ Tapes at Reduced Oxygen Partial Pressures" Physica C, **241**, 401 (1995).
14. L.A. Angurel, G.F. de la Fuente, A. Badía, A. Larrea, J.C. Díez, J.I. Peña, E. Martínez, R. Navarro en "Studies of High Tc Superconductors", 1996 World Scientific, Singapore
15. G. F. de la Fuente, J.C. Díez, L.A. Angurel, J. I. Peña, A. Sotelo, R. Navarro, Adv. Mater. **7**, 853 (1995).

Recibido: 31.05.01

Aceptado: 10.12.01