Chem. Mater. **1995,** *7,* 771–779

Superconducting $YBa_2Cu_3O_{7-\delta}$ Coatings by Simultaneous Electrodeposition of Y, Ba, and Cu in the Presence of Cyanide

S. Ondoño-Castillo, A. Fuertes, F. Pérez, P. Gómez-Romero, and
N. Casañ-Pastor*

Instituto de Ciencia de Materiales de Barcelona, C.S.I.C., Campus U.A.B., 08193 Bellaterra, Barcelona, Spain

Received November 23, 1994. Revised Manuscript Received January 23, 1995[⊗]

Simultaneous deposition in nonaqueous media (dimethyl sulfoxide) of Y, Ba, and Cu was achieved by electrolysis at constant potential in the presence of cyanide ions. Cyanide lowers the reduction potential for Cu to values near the reduction potentials for Y and Ba. Thus, an Y–Ba–Cu precursor is formed in situ over silver substrates, which upon an appropriate thermal treatment yields a $YBa_2Cu_3O_{7-\delta}$ coating; further annealing in oxygen renders the material superconducting. Depending on the substrate, the complexing agent, additives, and Y:Ba:Cu stoichiometric ratios in the bath, several impurities are detected. For the best deposits obtained, Y_2BaCuO_5 and CuO are present in small amounts. Potassium gets deposited along with Y, Ba, and Cu, but the oxidizing thermal treatment yields a coating with no traces of potassium present. After the thermal processing, the wires obtained present bulk superconducting properties. The particle size of $YBa_2Cu_3O_{7-\delta}$ in the final coating is about 10 μm. Intergranular connection is notable although the critical intergranular field is below 10 G. T_c values found are 92 K, the highest reported for $YBa_2Cu_3O_{7-\delta}$ prepared by this method on metallic substrates. Typical superconducting fractions are about 60%, and J_c values at liquid nitrogen temperatures are 51 A/cm^2 for deposits 96 μm thick over Ag substrates.

Introduction

It is well-known that the ceramic properties of superconducting copper oxides prevent their handling and mechanization into shapes needed for particular applications. Electrochemical methods are an especially attractive technique in this respect since they allow the preparation of deposits over metallic substrates of practically any shape and size, which after thermal treatment may yield the desired oxide, thus avoiding any further mechanical treatment.

The simplest approach consists in depositing the particles of the preformed oxide by electrophoresis. This technique, used traditionally to obtain deposits of alumina[1,2] or in corrosion protection,[3] has yielded already important results in the field of high-T_c superconductors.[4-12] In that case, the quality of the previously prepared powder and its particle size distribution are some of the main limiting factors.

An alternative approach is to prepare the oxide directly on the metal substrate by depositing the appropriate precursors onto the metal. The most favorable situation is found in cases where simultaneous codeposition of the elements at the atomic level takes place. To obtain those deposits, electrochemical methods may use the reduction to metals or to other insoluble species of the elements composing the final desired oxide. Focusing specifically on the preparation of $YBa_2Cu_3O_{7-\delta}$, a foreseen difficulty for the application of this technique to the obtention of superconducting coatings arises from the fact that all known superconducting cuprates contain elements that are very electropositive as compared to water or copper. Therefore, water must, in principle, be excluded. On the other hand, for any given overpotential applied, copper will tend to deposit much more easily than the other metals present in the superconductor. In the case of $YBa_2Cu_3O_{7-\delta}$, the amount of Y and Ba deposited is much smaller than that of Cu, when constant overpotentials are used. That occurs even after lowering the concentration of copper salts in solution to one-tenth or below the stoichiometric value.[10]

In principle the preparation of $YBa_2Cu_3O_{7-\delta}$ by electrodeposition from water may be considered difficult, if not impossible, given the larger reduction potential of water with respect to the reduction potential of yttrium and barium. However, some reports prove that it is

---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1995.

(1) Choudhary, J. Y.; Ray, H. S.; Rai, K. N. *Trans. J. Brit. Ceram. Soc.* **1982**, *81*, 189.

(2) Powers, R. W. *Am. Ceram. Soc. Bull.* **1986**, *65*, 1270.

(3) Pletcher, D.; Walsh, F. C. *Industrial Electrochemistry*, 2nd ed.; Chapman and Hall: London, 1990.

(4) Woolf, L. D.; Raggio, W. A.; Elsner, F. E.; Fisher, M. W.; Stephens, R. B.; Figueroa, T. L.; Shearer, C. H.; Rose, J. D.; Schaubel, K. M.; Olstad, R. A.; Ohkawa, T.; Duggan, D. M.; DiMartino, M.; Fagaly, R. L. *Appl. Phys. Lett.* **1991**, *58*, 534.

(5) Niu, H.; Shinkawata, H.; Hagiwara, Y.; Kishino, S. *Supercond. Sci. Technol.* **1991**, *4*, 229.

(6) Chu, C. T.; Dunn, B. *Appl. Phys. Lett.* **1989**, *55*, 492.

(7) Koura, N.; Shoji, H. *Physica C* **1991**, *190*, 163.

(8) Hein, M.; Müller, G.; Piel, H.; Ponto, L.; Becks, M.; Dlein, U.; Peiniger, M. *J. Appl. Phys.* **1989**, *66*, 5940.

(9) Nojima, H.; Shintaku, H.; Nagata, M.; Koba, M. *Jpn. J. Appl. Phys.* **1991**, *30*, L1166.

(10) Casañ-Pastor, N.; Gómez-Romero, P.; Fuertes, A.; Brossa, M. *Solid State Ionics* **1993**, *66*, 241.

(11) Mizuguchi, J.; Suzuki, M.; Yamato, H.; Matsumura, M. *J. Electrochem. Soc.* **1991**, *138*, 2942.

(12) Zhang, B.; Fabbricatore, P.; Gemme, G.; Musenich, R.; Parodi, R.; Risso, L. *Physica C* **1992**, *193*, 1.

0897-4756/95/2807-0771$09.00/0

possible to obtain deposits containing yttrium, barium, and copper in the form of hydroxides or oxides, from aqueous and DMSO−H_2O solutions containing no additives.[13,14] Those deposits have been obtained by co-deposition of the elements and after thermal treatment and annealing in oxygen atmosphere yield a large fraction of $YBa_2Cu_3O_{7-\delta}$. However, the observed physical properties are not satisfactory. Very low T_c values (≈40 K), for aqueous solutions and very low superconducting fractions in both aqueous and DMSO−H_2O solutions are observed.

Co-deposition from DMF solutions containing only the nitrates of yttrium, barium, and copper has also been reported,[15] using reduction potentials of −5 V vs Ag/AgCl. The final oxidized deposits have very low superconducting fractions and large amount of impurities containing the excess copper, such as CuO.

On the other hand, co-deposition at constant and pulsed potentials, from DMSO solutions of the nitrates of yttrium, barium, and copper, has been reported over ceramic and metallic substrates.[16−18] Applied potentials were −2.5 to −4 V vs $Ag/AgNO_3$, and pulsed sequences consisted of 1 s at −4 V followed by 1 s at −1 V. Transition temperatures were 74 K on Ni, 78 K on MgO, and 91 K on ZrO_2. The reports by these authors are the only ones mentioning measurements of critical current densities. J_c values at liquid He temperatures were ≈4000−5000 A/cm^2 on ceramic substrates and 500 A/cm^2 on Ni or Ag, when using pulsed potentials. The postannealed films contained sulfur impurities and the Y:Ba:Cu ratio of the superconducting films was far from 1:2:3.

In all cases mentioned above three electrode cells were used. In another report[19] a two-electrode cell with a potential difference of −423 V was applied on a 2-propanol solution containing the nitrates of these metals. Given the low conductivity of the medium, those high potentials were needed to carry current through the cell. As in water solutions, the deposit is formed by hydroxides that after heat treatment yield the superconducting oxide. T_c values obtained for single deposition experiments were 79 K and could be raised up to 88 K after successive depositions. Superconducting fractions were in the order of 13%.

The area of the electrodes used is rarely given. On the other hand, the deposition rates, when given, were in the order of 0.5 μm/min. Concentrations of the nitrates were around 0.05−0.1 M.

All reports previously made confirm the interest and large potential of electrochemical methods in the deposition of precursor films that upon heat treatment would yield the superconducting oxide. Part of the problems observed are caused by the large tendency of copper to get reduced to the metallic form, as compared with yttrium and barium, yielding copper-rich impurities in the final deposit. Other problems are related with the use of solvents more reducible than yttrium and barium.

In the search for a viable method, of technological interest, we have developed a new approach, reminiscent of some classical methods in electrochemistry. The use of additives that could modify the deposition potentials or kinetics of the metal under study is not new in industrial electrochemistry.[3] As we will show in this report, the preparation of $YBa_2Cu_3O_{7-\delta}$ precursors through co-deposition of precursors is an ideal case to apply this method.

Our approach implies modifying the copper deposition potential by formation of stable complexes of Cu^{+2} or Cu^{+} ions. If the complex formed is very stable, the reduction potential will shift toward the values of Y and Ba, thus favoring their simultaneous deposition. We have tested a series of amine, carboxylate, and cyanide ligands to assess the effectiveness of this approach for superconducting materials. It is worth mentioning that some of these ligands affect not only the reduction potential of the metal in question but also, when the free ligand is present in excess, its deposition kinetics.

The electropositive character of some of the elements involved requires the experiments to be performed in nonaqueous solvents. However, as discussed before, several groups including ours have shown that the presence of water may allow a possible alternative route that allows deposition of electropositive elements as amorphous hydroxides. Therefore, a rigorous exclusion of water is not needed.

Experimental Section

Our initial experiments were centered on the two recommended solvents for cathodic processes, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). We soon realized that we had worse solubility problems in the former, and so all work described in this paper is reported in DMSO.

Dimethyl sulfoxide (DMSO, 99% Merck) was used as purchased (maximum water content: 0.2%). $Y(NO_3)_3{\cdot}5H_2O$ (Aldrich 99.9%), $Ba(NO_3)_2$ (Merck 99%), and $Cu(NO_3)_2{\cdot}3H_2O$ (Merck 99.5%) were used to prepare the starting solutions. Only the barium nitrate was anhydrous, and it was not possible to dry the yttrium and copper nitrates without decomposition. KCN (Merck 97%) was used after washing with acetone. Glycine (Merck 99.7%), ethylenediamine (Fluka 99.5%), thiourea (Aldrich 99%), ethylenediaminetetraacetic acid (EDTA, Fluka 99.5%), and tetrabutylammonium cyanide (TBACN, Merck 96%) were used as purchased. Platinum (99.9%), silver (99.99%), and copper (99.99%) wires from Goodfellow were used after washing with hydrochloric acid and acetone. Tetrabutylammonium chloride (Fluka, 97%) was used as purchased. DMSO solutions of the nitrates were prepared fresh every day and electrochemical experiments were carried out in argon atmosphere.

Cyclic voltammograms and electrolyses at constant potential were run on a single-compartment cell using a potentiostat/galvanostat EG&G PAR 273A interfaced to a PC and controlled by EG&G PAR 270 software. The working electrode was the metal wire serving as substrate. The substrates initially used were Pt, Cu, and Ag wires; the first two were electroplated with Ag prior to their use. Given the lack of superconducting properties observed for deposits on Pt and Cu,[10] all experiments were carried out on Ag substrates. Three-electrode cells were used. Platinum wire 0.50 mm in diameter was used as counterelectrode. The reference electrode was a Ag/AgCl double-junction electrode (1 M tetrabutylammonium chloride (TBACl) in DMSO filling the bridge). All deposition experiments were run at constant potential to avoid sequential deposition of the elements. The stoichiomet-

---

(13) Slezak, P.; Wieckowski, A. *J. Electrochem. Soc.* **1991**, *138*, 1038.

(14) Minoura, H.; Naruto, K.; Takano, H.; Haseo, E.; Sugiura, T.; Ueno, Y.; Endo, T. *Chem. Lett.* **1991**, 379.

(15) Weston, A.; Lalvani, S.; Naushad, A. *J. Mater. Sci.: Mater. Electron.* **1991**, *2*, 129.

(16) Bhattacharya, R. N.; Parilla, P. A.; Mason, A.; Roybal, L. L.; Ahrenkiel, R. K.; Noufi, R.; Hellmer, R. P.; Kwak, J. F.; Ginley, D. S. *J. Mater. Res.* **1991**, *6*, 1389.

(17) Bhattacharya, R. N.; Noufi, R.; Roybal, L. L.; Ahrenkiel, R. K. *J. Electrochem. Soc.* **1991**, *138*, 1643.

(18) Bhattacharya, R. N.; Parilla, P. A.; Noufi, R. *J. Electrochem. Soc.* **1992**, *139*, 67.

(19) Abolmaali, S. B.; Talbot, J. B. *J. Electrochem. Soc.* **1993**, *140*, 443.

ric ratios used in the DMSO solution were empirically adjusted, for each potential, in order to achieve the appropriate Y:Ba:Cu ratio in the final oxide, as deduced by the impurities present in X-ray powder diffractomgrams. Different concentrations of additives and ligands were also used in the process of optimization. The concentrations given in Tables 1 and 3 are optimal for each particular media. Metallic substrates used had an area of 0.4 cm^2 exposed to the DMSO solution. The length of wire covered was typically 3 cm. Although other potentials were used in different media, typical applied potentials were between −2.5 and −2V vs Ag/AgCl. The deposition rates were of the order of 1.5 μm/min measured in terms of the thickness of the final superconducting deposit. Usual deposit thickness was 200 μm after 2 h of deposition. Typical current efficiency values in terms of Y, Ba, and Cu deposition were 66%, and 80% in terms of the total amount of material deposited. A typical current during the electrolysis was 9 mA, with current densities of the order of 2.3 A dm^{-2}. Once coated with the complex metallic precursor, the wires were thermally treated at 900 °C in air for 12 h and annealed at 450 °C for 12 h in flowing oxygen. Heating rates were 300 °C h^{-1}.

Magnetic measurements were performed with an AC Lakeshore susceptometer. Critical current measurements were performed at liquid N_2 temperatures using the four-point method and using a signal of 1 $\mu V\ cm^{-1}$ as a criterion of nonzero resistance. X-ray diffraction patterns were obtained with a Rigaku D/MAX-RC diffractometer using Cu Kα on powder samples taken from the deposits. Scanning electron microscopy experiments were performed on a Hitachi S-570 microscope. EDX analyses were performed on a JEOL JSM 840 scanning electron microscope. ESR X-band experiments were performed at room temperature on a Brucker 300E spectrometer.

Thermal analyses were carried out on a Perkin-Elmer TGA7 thermal balance under O_2 flow. The intermediates present at each plateau were studied by performing thermal treatments on standard tubular furnaces under controlled oxygen atmosphere. Elemental C, N, S analyses were carried out in a Carlo Erba CHN EA 1108 analyzer (maximum combustion temperature 1800 °C). Potassium qualitative analysis were performed in water with sodium tetraphenylboron. Barium qualitative analyses were performed in water with sodium sulfate.

Results and Discussion

Preliminary Experiments. When deposition at constant potential from DMSO solutions containing copper, yttrium, and barium are carried out in absence of any additive, copper is deposited preferentially, as expected, yielding an excess of copper oxide in the final deposit even for low copper concentrations in the starting solution.[10,20]

A preliminary study of the deposition potentials for each element has been carried out by running cyclic voltammograms of solutions containing the nitrate salts of the individual ions in DMSO, in the absence and presence of several complexing agents.

Reported reduction potentials in DMSO for Cu^{2+} and Ba^{2+} are around 0 and −2.2 V, respectively.[21] Accordingly, we observe reduction waves for copper, barium and yttrium with maxima at −0.2, −2.3, and −2.4 V, respectively, vs Ag/AgCl, in the absence of additives or complexing agents. See Figure 1.

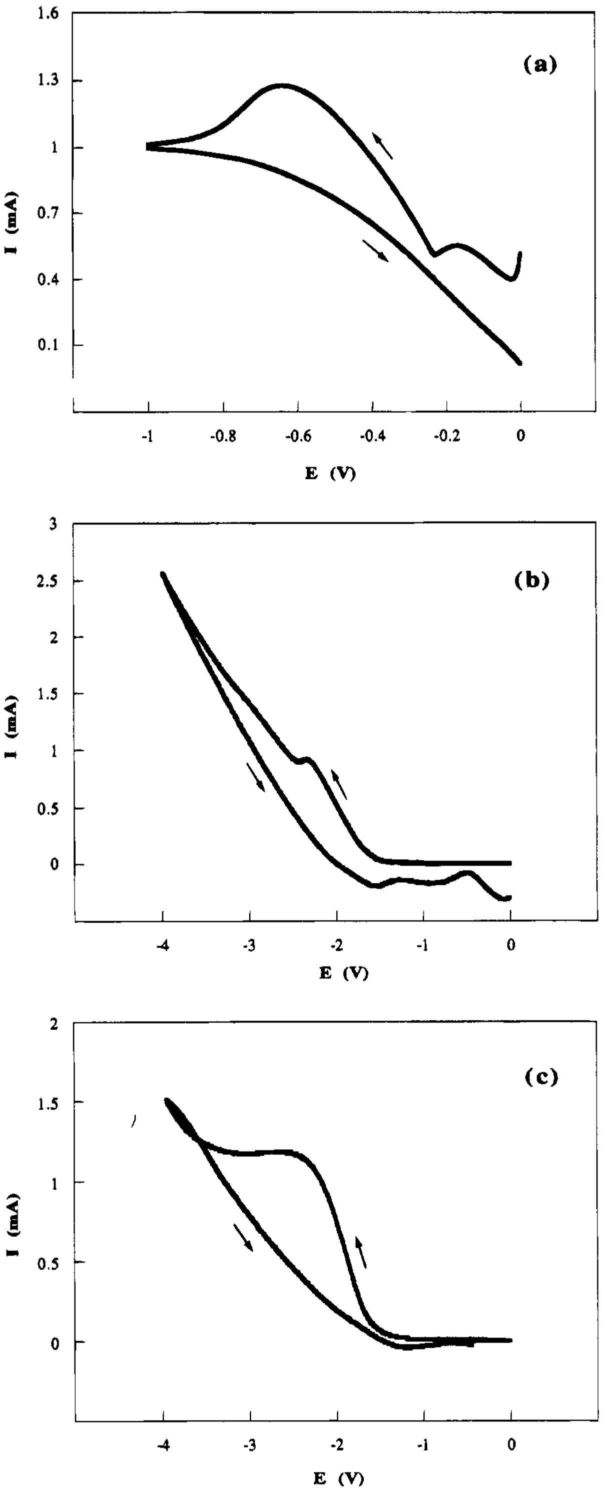

Figure 1. Cyclic voltammograms (60 mV/s) in DMSO (0.03 M TBACl) of (a) 3 × 10^{-2} M $Cu(NO_3)_2{\cdot}3H_2O$; (b) 6 × 10^{-2} M $Ba(NO_3)_2$; (c) 5 × 10^{-2} M $Y(NO_3)_3{\cdot}5H_2O$.

Independent deposition of each of the elements is possible from solutions containing each of the respective nitrates. In the case of Y and Ba, with applied E = −2.25 V vs Ag/AgCl, the substrate has metallic appearance not distinguishable from the metallic substrate, when taken out of solution. The current that passes through the cell increases during deposition agreeing with the formation of a deposit of metallic character. Only after being exposed to air for some time, a white deposit can be observed. When independent Ba deposition is tested, qualitative tests with sulfate yield positive for the presence of Ba in such deposit. If the deposit is immersed rapidly in water after deposition, a gas is released, indicating that Ba is deposited in a reduced

---

(20) Ondoño-Castillo, S.; Perez, F.; Fuertes, A.; Gomez-Romero, P.; Casañ-Pastor, N. *Physica C* **1994**, *235–240*, 3411. (Proceedings of the M2S-HTSCIV, Grenoble 1994).

(21) Koch, T. R.; Purdy, W. C. *Talanta* **1972**, *19*, 989.

form, either as an organometallic complex or in metallic form. (Although in the past the release of gas upon reaction with water has been considered a good indication of the existence of the metal in its reduced form, caution has been recommended by some authors, for whom the possibility of formation of organometallic species has a high probability.[22]) On the other hand, the same tests carried out with Y yield very irreproducible results when the deposition of Y is carried out independently. However, once the simultaneous deposition of Y, Ba, and Cu is accomplished, the amount of Y in the final deposit is very reproducible.

Copper can also be deposited independently, yielding black, fine particle deposits for large current densities and good-quality copper colored deposits for small currents.

When complexing agents are used, the yttrium and barium waves shift only slightly toward more negative values (0.1–0.2 V), while copper shows little change in the case of amines, and a considerably large shift in presence of cyanide (see Figure 2). Table 1 shows the reduction waves observed for copper nitrate solution in DMSO in the presence of some additives and complexing agents. In all cases, copper deposition is observed for the first reduction wave. In the case of KCN, the first wave involves deposition of both copper and potassium. The existence of several waves may be also ascribed to the presence of an equilibrium among different complexes within the solution and to the possible reduction of some of the complexing agents or nitrates.

Cyclic voltammograms of KNO_3 in DMSO show no reduction wave before that of potassium (see Figure 3). On the other hand, TBACN in the presence of copper nitrate shows no reduction wave before the wave corresponding to the solvent DMSO. It seems, therefore, that nitrate ions do not interfere down to −2.25 V vs Ag/AgCl.

As a less toxic alternative to the use of cyanide, we also studied the effects of sulfamic acid, H_2NSO_3H, reagent that has replaced cyanide in some industrial processes.[3] Our observations imply that in DMSO, if any complex is formed, the deposition of metallic copper is not hindered or even modified with respect to the cases where no complexing agent is present.

On the basis of the reported CV, simultaneous depositions of Y, Ba, and Cu were carried out in the presence of various complexing agents. With the exception of solutions containing cyanide, the final deposits contained large amounts of impurities, as shown in Table 3 with a few examples. For that reason, research was pursued using cyanide as complexing agent, in which case the deposition potentials of the three metals are closer.

Study of the Complexes Present in DMSO Containing Cu^{2+} and CN^-. Depending on the solvent, temperature, and copper-to-cyanide ratio, different complexes have been observed.[23–27] The identity of each complex, however, remains unclear. In water, for example, CN^- forms an insoluble precipitate with Cu^{2+} that decomposes into CuCN, or $[Cu(CN)_2]^-$ if there is excess CN^-, and cyanogen, $(CN)_2$.[24] A metaestable purple complex, $Cu[Cu(CN)_4]^{2-}$, is formed before the redox reaction when CN^- is added to Cu^{2+} solutions. In cold methanol or DMF solutions, a soluble purple Cu^{2+} complex is stable for which several identities have been proposed, all involving four CN^- per Cu^{2+}.[23]

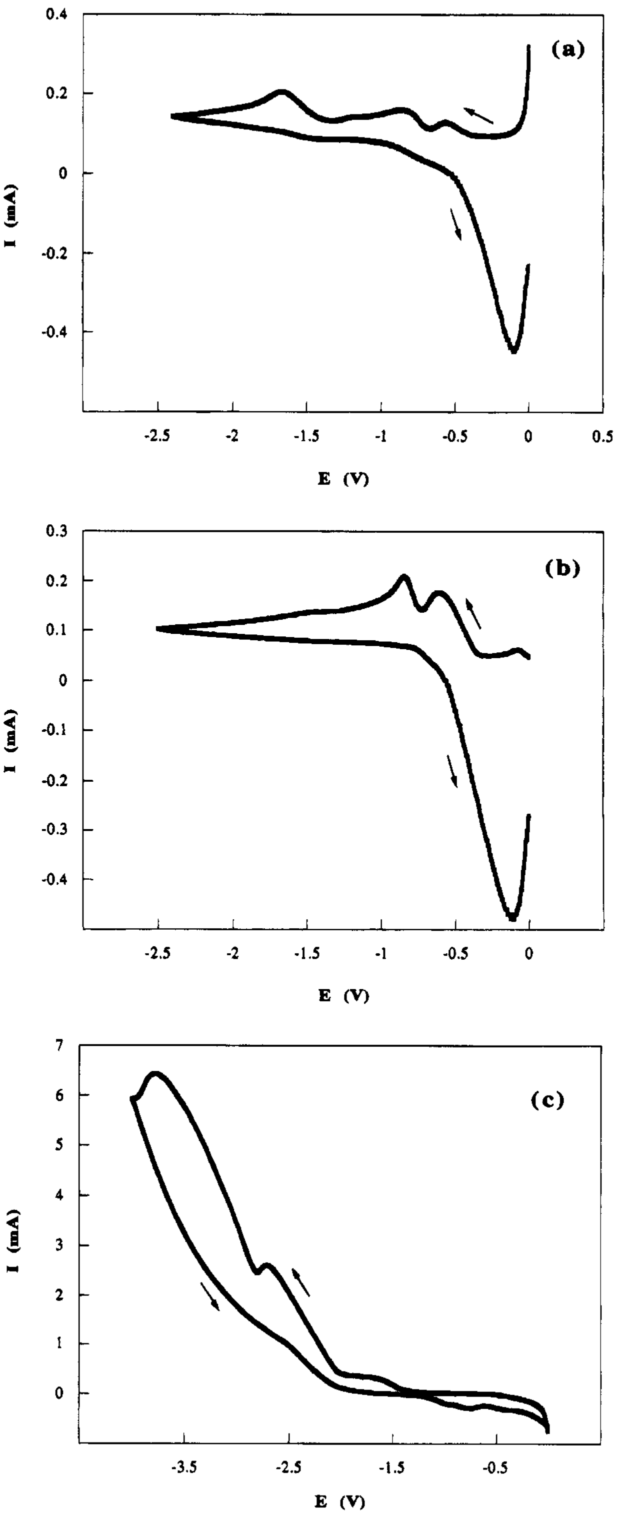

Figure 2. Cyclic voltammograms for 0.01 M $Cu(NO_3)_2 \cdot 3H_2O$ in DMSO (0.03 M TBACl) in presence of various ligands: (a) 0.1 M glycine, 20 mV/s; (b) 0.1 M ethylenediamine, 20 mV/s; (c) 0.155 M KCN, 200 mV/s.

Our experiments in DMSO show the exothermic precipitation of a brown solid when KCN is added to copper nitrate solutions, accompanied by the simultaneous evolution of a gas. This precipitate dissolves in

---

(22) Brenner, A. *Adv. Electrochem. Electrochem. Eng.* **1967**, *5*, 205.

(23) Longo, A.; Buch, T. *Inorg. Chem.* **1967**, *6*, 556.

Table 1. Reduction Waves Observed in Cyclic Voltammetry Experiments of Copper Nitrate Solutions in DMSO (Values Correspond to Wave's Maxima)

electrolyte	complexing agent	E (V vs Ag/AgCl)
none	none	−0.2/−0.67
TBACl 0.03M	none	−0.4/−1.25
none	glycine (0.1 M)	−0.45/−0.96/−1.61
TBACl 0.03M	glycine (0.1 M)	−0.32/−0.81/−1.44
TBACl 0.03M	ethylenediamine (0.1 M)	−0.70/−0.91/−1.42
none	sulfamic acid (0.1 M)	−0.4/−0.7
none	KCN (0.155 M)	−2.33/−2.77
TBACl 0.03M	KCN (0.155 M)	−2.12/−2.73
none	TBACN (0.155 M)	none

Table 2. Elemental Analyses of Solids Isolated from a DMSO Solution That Contains the Copper Cyanide Complex under Study

	%C	%N	C/N ratio
solid A, washed abundantly with H_2O	25.91	29.47	1.03
solid B, washed with H_2O	12.36	17.93	0.80
calcd for $K_2Cu(CN)_3$	16.38	19.11	1.00
calcd for $K_2Cu(CN)_4$	19.54	22.79	1.00
calcd for $K_2Cu(CN)_3$:KNO_3 (weight % 75:25)	12.29	17.80	0.90
calcd for $K_2Cu[Cu(CN)_4]$	20.2	23.6	1.00
calcd for $K_2[Cu(CN)_4(HCN)]$	22.0	25.7	1.00

excess CN^- ($[CN^-]/[Cu^{2+}] = 4$) yielding a very intense colored orange-red solution whose cyclic voltammogram (CV) is shown in Figure 2c (see also Table 1). When cyanide is added to potassium nitrate solutions, no gas evolution is observed; therefore the observed gas must come from reaction of cyanide with Cu^{2+}. Higher concentrations of potassium cyanide in DMSO corresponding to a ratio CN^-/Cu^{2+} larger than 4 cannot be reached with KCN because the latter does not dissolve beyond the amount needed to form the cyanide complex with copper.

In an attempt to identify the nature of the existing complex in DMSO solutions, we have carried out its precipitation (drying and washing with water) which yields a solid that is paramagnetic. This paramagnetism corresponds to a very small fraction of free Cu^{2+}, 0.7% at 5 K. On the other hand, ESR experiments on copper nitrate solutions without cyanide show the existence of a Cu(II) signal that disappears when cyanide is added.

The red DMSO solution is stable indefinitely, and the color is preserved when water is added. This lack of reactivity against water seems to imply the absence of Cu^{2+}, since this will react with cyanide in aqueous solutions. On the other hand, it is not possible to get the red complex starting from Cu^+ solutions. CuCN does not dissolve in DMSO, until KCN is added to achieve a final $CN^-/Cu^+ = 3$. The resulting solution is beige colored. At this point, a possible explanation to account for all data observed will be the existence of a mixed-valent complex containing copper in both oxidation states. The red color of the complex could be derived from an intervalence charge-transfer band located at the upper energy range of the visible spectrum, involving a mixed-valent compound with a high degree of electron localization.

Electrogravimetric studies at constant −2.25 V vs Ag/AgCl were initially performed in an attempt to evaluate the oxidation state of copper present in solution. However, it was impossible to separate potassium and copper deposition. The deposit always contained a significant amount of potassium as detected with sodium tetraphenylboron.

Precipitation of the complex by evaporation of the solution to dryness yields sulfur-free solids that contain KNO_3 in different amounts depending on the amount of water used in rinsing. Water dissolves potassium nitrate but also a considerable portion of the red complex. The solid residue is brown-black and elemental analyses yield the values described in Table 2 for solid A. The weight percent of C and N for this solid are very high, 25.91% and 29.47%, respectively, with a C/N ratio equal to 1, indicating the existence of cyanide that must be in a proportion of at least 3 CN^- per copper ion. On the other hand, solids rinsed with smaller amounts of water yield much lower values for carbon and nitrogen analysis. If the amount of nitrate is deduced from the difference between carbon and nitrogen analysis, we obtain typically 20−25% of KNO_3 in the solid (solid B in Table 2) and therefore we can induce an estimated value for carbon content in the cyanide complexes of 15.5%. This value corresponds however to a weighted average of carbon present in the black solid and in the red complex.

The difficulties found in trying to establish the oxidation state of copper in the complex present in DMSO were also found by other authors observing the purple complex, in the literature.[23−27] The different colors and the instability of the purple complex in the presence of water shows that the purple and red complexes are very different. It has been proposed that copper(II) cyanide complexes may be greatly stabilized by participation in the coordination sphere of good σ-bonding ligands. In that sense, DMSO cannot be considered an innocent solvent and could indeed coordinate to copper. However, no sulfur is detected after precipitation of the complex to dryness. On the other hand, the lack of magnetic properties at room temperature (ESR) and 5 K (SQUID measurements) are consistent with either a Cu(I) monomeric complex or a Cu(II) dimmer with strong antiferromagnetic interaction among coppers. In fact, we may propose, on the basis of magnetism and elemental analysis, the existence of a new complex, with a ratio $CN^-/Cu = 3$ or 4. Further work is being carried out to elucidate its nature.

The stability of this particular copper cyanide complex may be the main factor causing the large shift in the copper reduction potential, and their negative charge may account for the strong inhibition of copper deposition observed. (Nevertheless, it is also possible that the formation of a Cu−K alloy may also shift notably its deposition potential. However, EDX analysis of a fresh deposit obtained from a copper−KCN solution, shows the existence of separate crystals containing either Cu or K.)

Depositions from Cyanide Media in the Absence of Potassium: TBACN. Despite the existence of K codeposited, the final oxidized material does not contain any trace of it, given the high volatility of potassium oxidation products, although the morphology of the deposit, as discussed later, presents large holes probably caused by the release of potassium in the final stages.

---

(24) Massey, A. G. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Ed.; Pergamom Press: Oxford, 1973; Vol. 3, Chapter 27.

(25) Griffith, W. P. *Q. Rev.* **1962**, *16*, 188.

(26) Chadwick, B. M.; Sarpe, A. G. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 83.

(27) Glasner, A.; Asher, K. R. S. *J. Chem. Soc.* **1949**, *4*, 3296.

Table 3. Deposits Obtained over Ag Wire after Thermal Treatment at 900 °C (123 Stands for $YBa_2Cu_3O_{7-\delta}$; 211 Stands for Y_2BaCuO_5) (Content of Each Phase Based on X-ray Diffraction Intensities of the Maximum Peaks)

Y:Ba:Cu (mM) starting conc	applied *E* (V) vs Ag/AgCl	solvent	additives	123:211:CuO:$BaCO_3$ from X-ray
40:70:95	−4	DMSO	thiourea	100:−:50:−
40:70:95	−4	DMSO	ethylenediamine	10:−:100:−
9.8:14.8:156	−2.25	DMSO	KCN, TBACl	100:16:10:−
9.8:15.5:156	−2.25	DMSO	KCN, TBACl	100:6:9.5:−
9.8:15.9:156	−2.25	DMSO	KCN, TBACl	100:9:4:−
20:40:60	−2	DMSO−10%H_2O		100:−:32:−
20:40:60	−2	DMSO−10%H_2O	ethylenediamine	80:−:64:−
20:40:60	−2	DMSO−10%H_2O	thiourea	10:−:100:−

In an attempt to deposit copper from this copper cyanide solution in the absence of potassium, TBACN has been used as an alternative reagent to KCN in solutions containing only copper nitrate. The resulting solution has the same red color after the ratio $CN^-/Cu^{2+} = 4$ is reached. The corresponding CV shows no reduction waves before the reduction of the solvent, DMSO. If we consider KCN and TBACN to be completely ionized in DMSO, the same copper cyanide complex is formed and the reduction potential for copper must remain at the same value. The fact that no waves are observed down to −2.5 V implies that potassium deposition was responsible for the reduction wave above −2.25 V and that it is the reduction of potassium what induces the deposition of copper. As a result, codeposition of Y, Ba, and Cu in presence of TBACN is more difficult and no acceptable deposits have been obtained to date.

Passivation Problems. Throughout this work, several problems related with electrode passivation have been found. The mechanism of deposition of Y and Ba, when the process is carried out independently, goes through reduction to the metallic state (or to an organometallic) at least down to −2.25 V vs Ag/AgCl. For potentials below that value, passivation of the working electrode is observed, with very low electrolysis currents and the formation of nonmetallic deposits that do not react with water. Very possibly at these high overpotentials, either hydroxide (formed in the electrolysis of the water present) or dimethyl sulfides (from the DMSO reduction) of Y^{3+} and Ba^{2+} are formed on the surface of the electrode. Despite the problems found in the independent deposition of Y (and sometimes Ba), the simultaneous electrodeposition of the three elements follows a much more reproducible track. It is known that the kinetics of deposition usually vary when several elements are being co-deposited.[28] The reason for that variation may be as simple as changes in activities of the different ions near the cathode or as complex as the formation of solid solutions or intermetallic compounds.

To evaluate the influence of water content on those passivation problems, several experiments were carried out with controlled amounts of it. Despite the logic assumption that rigorous absence of water is needed, we observed that, on the contrary, when no complexing agents are present, a controlled amount of water seems to help the obtention of $YBa_2Cu_3O_{7-\delta}$. When DMSO was dried with activated alumina and in the absence of any complexing agent, a small proportion of $YBa_2Cu_3O_{7-\delta}$ was observed in the deposit for any applied potential. For DMSO−10% H_2O, a dramatic change is observed and the amount of $YBa_2Cu_3O_{7-\delta}$ in the final oxide increases notably. If the same 10%H_2O solutions contain ethylenediamine, the same result is observed (see Table 3). It is very probable that, at the applied potentials, the reduction of water that occurs simultaneously with copper deposition creates a local excess of OH^- ions near the cathode that precipitate Y and Ba (as their hydroxides) on the surface. In the presence of thiourea, however, the effect is opposite, mainly because of the large deposition of copper. On the other hand, in the presence of cyanide, two types of behavior are observed: at low water concentrations, the working electrode gets passivated below −2.25 V vs Ag/AgCl, and the deposition is inhibited by the formation of a dense insulating phase, while above 10% water the current during deposition increases again, probably due to the reduction of water that causes hydrogen evolution and formation of hydroxides at the electrode. For low water contents and in presence of KCN, the most hydrated and hygroscopic salt, $Y(NO_3)_3 \cdot 5H_2O$, is responsible for the passivation, as has been proven in several experiments with sequential addition of the reactants. It is therefore very important to control the hydration degree of this salt.

Deposits Obtained in DMSO−KCN Media. Properties and Microstructure. A summary of optimal results obtained in co-deposition experiments with KCN are shown in Table 3. Even in the absence of any additive, a small proportion of superconducting $YBa_2Cu_3O_{7-\delta}$ is observed, after a thermal treatment at 900 °C and annealing at 450 °C. All wires are bulk superconductors when silver substrates are used.

Optimal deposits are obtained from KCN solutions and show that the majoritary phase is $YBa_2Cu_3O_{7-\delta}$ while a small amount of Y_2BaCuO_5 and CuO (≈10−15% in total) is present. The existence of these phases in this proportion do not present an important problem. It is known that some impurities, particularly Y_2BaCuO_5, act as pinning centers for the $YBa_2Cu_3O_{7-\delta}$ improving its transport properties.[29,30]

Additives typically used in water to improve the quality of copper deposits (thiourea, ethylenediamine, etc.) also favor the preferential deposition of metallic copper in DMSO over that of yttrium and barium, despite the existence of cyanide, leading to excess copper in the final oxide in form of CuO.

In terms of their physical properties, the best coatings obtained are those from DMSO solutions containing KCN as the only additive. For them, superconducting

---

(28) Faust, C. L. In *Modern Electroplating*, 3rd ed.; Lowenheim, F. A., Ed.; John Wiley & Sons: New York, 1973; Chapter 18.

(29) Jin, S.; Tiefel, T. H.; Kammlott, G. W. *Appl. Phys. Lett.* **1991**, *59*, 540.

(30) Murakami, M.; Gotoh, S.; Fujimoto, H.; Yamaguchi, K.; Koshizuka, N.; Tanaka, S. *Superconduct. Sci. Technol.* **1991**, *4*, S43.

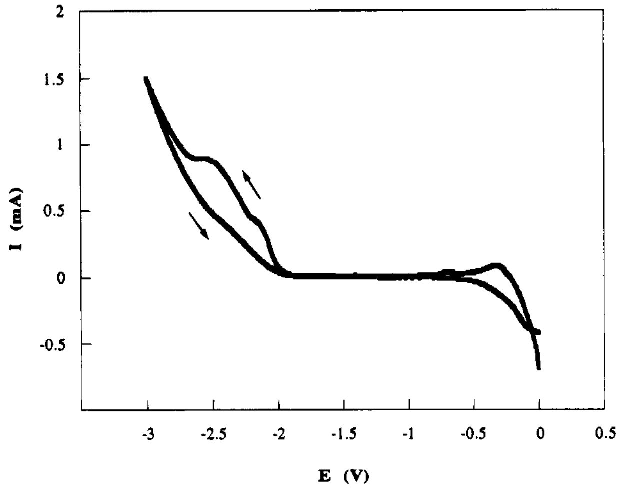

Figure 3. Cyclic voltammogram of 3×10^{-2} M KNO_3 in DMSO (0.03 M TBACl), at 100 mV/s.

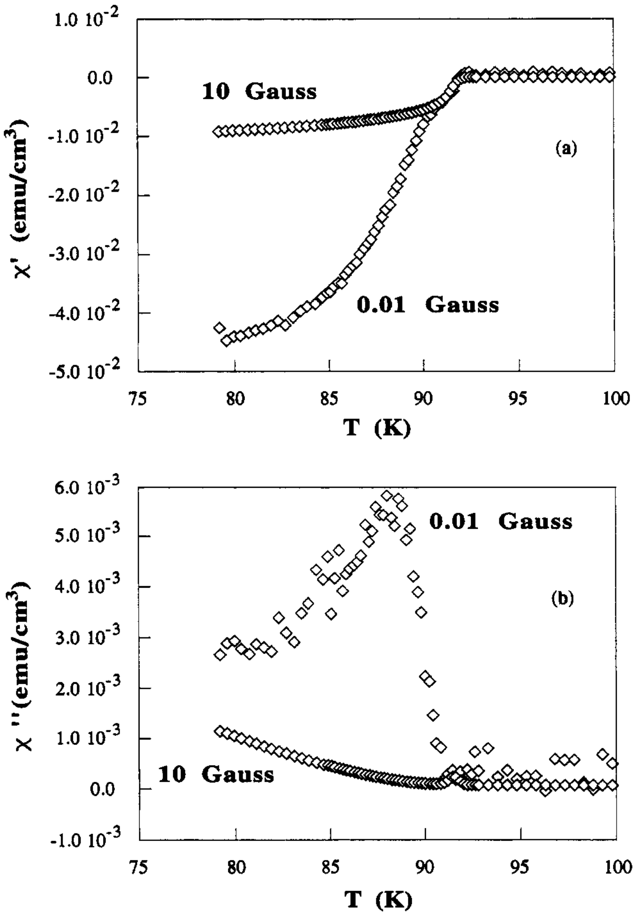

Figure 4. Ac magnetic susceptibility of a deposit obtained from DMSO (KCN; Y:Ba:Cu = 10:16:156 mM, cyanide/copper = 4) oxidized at 900 °C and annealed at 450 °C in oxygen. (a) In-phase susceptibility, χ'. (b) Out-of-phase susceptibility, χ''.

Table 4. Elemental Analyses for Deposits Treated at Different Temperatures in O_2

temp (°C)	%N	%C	%H	%S
as deposited	0.96	4.43	1.36	0
350	0.56	3.43	0.21	0
720	0	2.90	0.21	0
840	0	0.10	0	0

fractions are ≈60%, according to ac susceptibility data (see Figure 4), with $T_c = 92$ K. Both the in- and out-of phase components of the magnetic susceptibility are highly dependent on the applied ac field, down to liquid N_2 temperature. The dependence of the in-phase component, χ', indicates that intergranular connection exists at 0.01 G but that it is not appreciable at 10 G. However, a closer look at the out-of-phase component shows that the maximum in χ'' at 0.01 G related to intergranular connection appears to exist also at 10 G but at lower temperatures as reflected in the increasing slope of χ'' vs T. Therefore, the grain connectivity, although present, is not optimal. The small amount of carbon present in the final deposit (see Table 4) may account in part for this lack of grain connectivity, but more important is the fact that the thermal treatments have been limited to 900 °C because of the substrate (Ag) melting point. The optimal sintering temperature to connect the grains is around 1000 °C. This large thermal difference is more likely to be responsible for the low intergranular connection.

Critical current measurements show low but significant values at liquid N_2 temperatures. J_c values observed in the absence of magnetic fields are 51 A/cm^2 at liquid N_2 temperatures. They are comparable if not superior to the only values previously reported of 500 A/cm^2 at a much lower temperature, liquid He, for deposits obtained by pulsed methods (no T_c reported) on Ag substrates.[16-18]

In summary then, our observed T_c values are the highest reported on samples obtained by electrodeposition on metallic substrates. These high values may be caused by the characteristics of the precursors obtained in the presence of cyanide. Thermal factors may also influence considerably the final T_c values. There are considerable differences among authors in the thermal treatment of the precursors after deposition. Previous reports on Ag substrates reach temperatures such as 850 °C, while in this work we heat up to 900 °C. On the other hand, we maintain the deposit at this temperature for 12 h instead of the 45 min reported by Bhattacharya, for example.[16-18] The good results observed here may be the result not only of the use of KCN but also of a more prolonged thermal treatment that allows for a better crystallization of $YBa_2Cu_3O_{7-\delta}$ particles.

Figure 5 shows electron scanning microscopy pictures of wires obtained in KCN media, both as deposited and after thermal treatment. They correspond to the same sample for which the susceptibility is shown in Figure 4. EDX analysis show that the large plates (~10 μm) are $YBa_2Cu_3O_{7-\delta}$, while the small spheres (~1 μm) correspond to the so-called green phase, Y_2BaCuO_5. Crystals of CuO are present in small amounts with the same morphology as those of $YBa_2Cu_3O_{7-\delta}$. Contrary to the inner part of the deposit, in which large sponge-like holes are observed, its surface is homogeneous and well connected.

Deposits Obtained in DMSO–KCN Media. Thermal Analysis. The mechanism of $YBa_2Cu_3O_{7-\delta}$ formation by oxidation of the deposit and decomposition and reaction of the precursors was followed by thermal gravimetry in flowing oxygen. Several small weight gains may be observed below 300 °C overlapped with large weight losses. Those are followed by a large and sometimes violent weight loss above 720 °C that appeared to have two components. In an attempt to separate them and to lower the violence of the process,

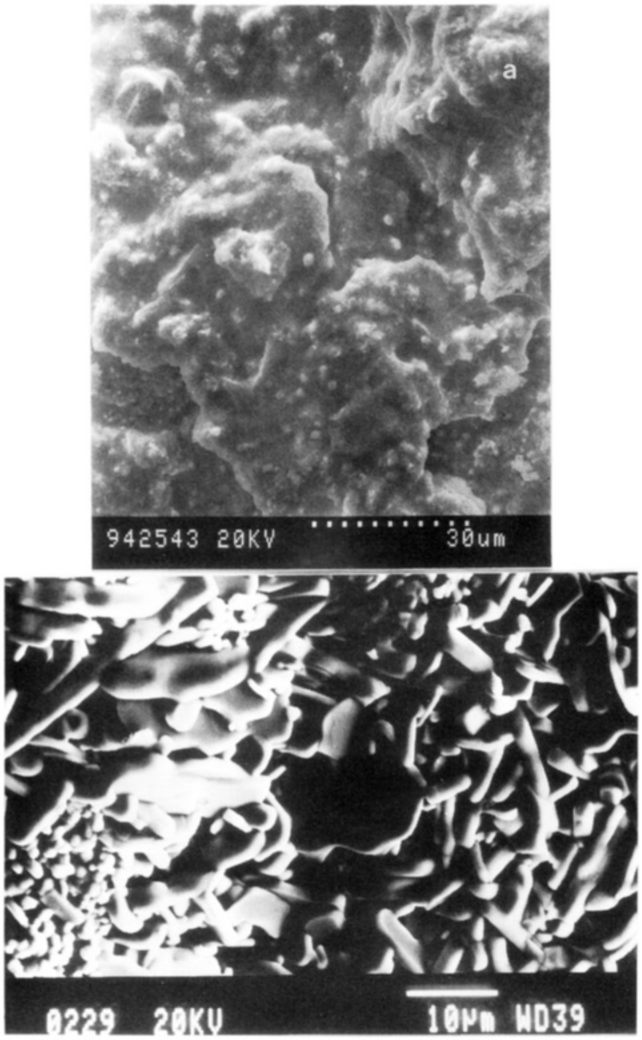

Figure 5. Scanning electron microscopy photographs of deposits obtained from cyanide solutions. (Y:Ba:Cu = 10:16:156 mM, cyanide/copper = 4). Longitudinal view. (a, top) As deposited; (b, bottom) oxidized at 900 °C and annealed at 450 °C in oxygen. Platelets are $YBa_2Cu_3O_{7-\delta}$, spheres are Y_2BaCuO_5.

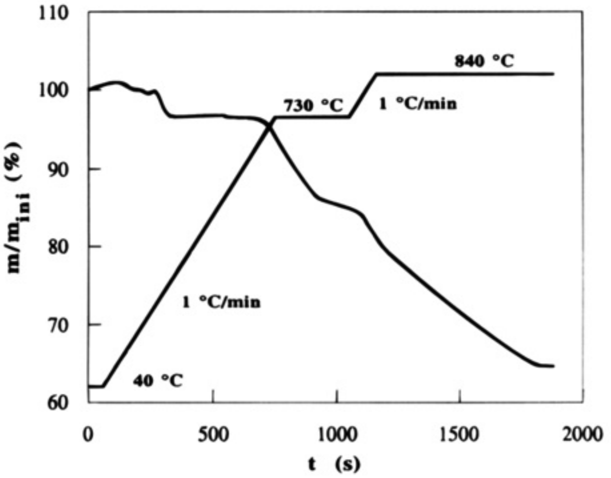

Figure 6. TGA in O_2 of a deposit obtained from a DMSO solution containing cyanide. (Y:Ba:Cu = 10:16:156 mM, cyanide/copper = 4). Heating rate = 1 °C/min.

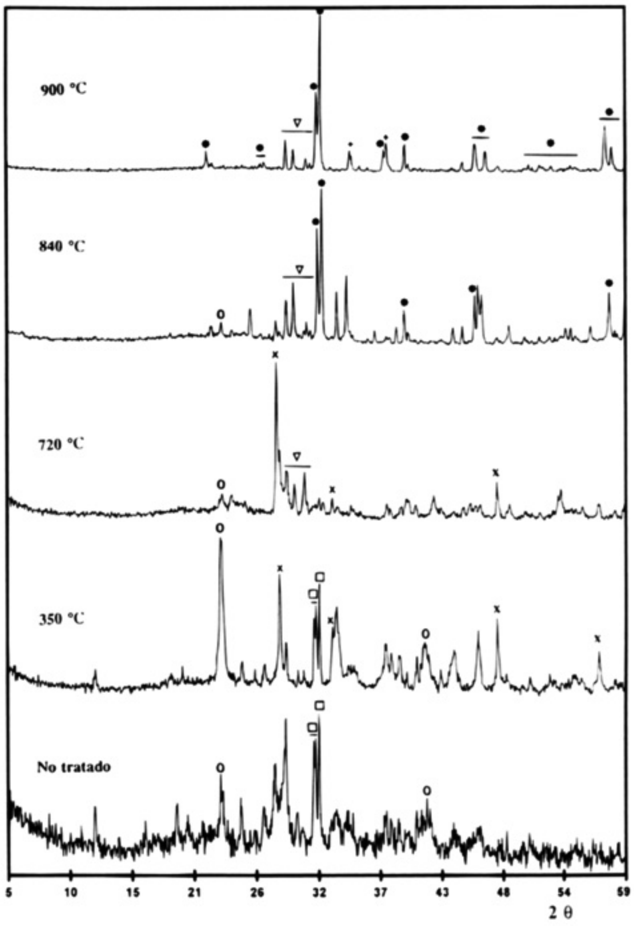

Figure 7. X-ray diffraction patterns of deposits obtained from DMSO solution (Y:Ba:Cu = 10:16:156 mM, cyanide/copper = 4), treated at several temperatures in O_2. (○) $BaCO_3$; (□) $K_2CO_3{\cdot}1.5H_2O$; (×) Y_2O_3; (+) CuO; (*) orthorhombic $YBa_2Cu_3O_{7-\delta}$; (▽) Y_2BaCuO_5.

a plateau was imposed at 730 °C, and the speed was lowered to 1 °C/min. The results of this experiment are shown in Figure 6. Only in this case the speed of the violent reaction is lowered and the weight loss can be evaluated. Below 300 °C, 4% of the weight is lost, an amount easily assignable to adsorbed water or solvent from the deposition medium as well as to the hydration water of the carbonates that may form upon exposure of the deposit to air. Potassium and barium carbonates and potassium peroxide or superoxide decompose above 700 °C, which leads to a large weight loss. The total weight loss before $YBa_2Cu_3O_{7-\delta}$ is formed is 36% while loss from carbonated barium or yttrium accompanied by copper oxidation can only account for 10−15% of the weight loss. This implies a large amount of potassium species present in the original deposit.

To identify the intermediate species existing at each temperature the deposit was treated at 350, 720, and 840 °C in flowing oxygen. X-ray powder diffraction patterns and elemental analyses of the products obtained are shown in Figure 7 and Table 4.

According to X-ray data and despite the existence of nonidentified phases in the lower temperature samples, it can be observed that the barium and potassium present in the deposit get carbonated at room temperature, by reaction with atmospheric CO_2. At 350 °C, those two carbonates and Y_2O_3 are observed. At 720 °C, the presence of Y_2BaCuO_5 is already evident, while at 840 °C orthorhombic $YBa_2Cu_3O_{7-\delta}$ is formed. Finally, at 900 °C, the reaction is complete, showing $YBa_2Cu_3O_{7-\delta}$ as the major phase and small amounts of CuO and Y_2BaCuO_5.

Elemental analyses show that the deposit as obtained at room temperature and dried under vacuum does not contain any trace of sulfur, and therefore there is no DMSO adsorbed. On the other hand, it shows small amounts of carbon and nitrogen (Table 4) that correspond to the potassium and barium carbonates, to some nitrates or even cyanides adsorbed. The nitrates start to decompose below 350 °C and are absent at 720 °C, while some carbonates are still present at 720 °C. The disappearance of peaks related to potassium phases at this temperature seems to imply that the violent weight loss is related to the decomposition and evaporation of potassium carbonate and/or peroxide or superoxide. The final deposit does not contain nitrogen and contains only traces of carbon. Small amounts of carbon impurities are usual when carbonates or organic precursors are used in the synthesis of oxides.[31] If present in sufficient amount, they may affect intergranular connection and therefore may affect the transport properties of the material. As discussed above, however, the large difference between the used sintering temperature and the optimal of 1000 °C seems more likely to be the reason for problems in grain connection.

It appears from the observed thermal behavior of the deposit that the reaction occurs through decomposition of carbonates and nitrates into binary oxides that later form the green phase, Y_2BaCuO_5. This, in turn, reacts with more binary oxides, yielding $YBa_2Cu_3O_{7-\delta}$ at 840 °C. We want to point out that the usual temperature of formation of this oxide by the ceramic method is above 900 °C. Its formation at lower temperatures by the method described suggests some similarity with other soft-chemistry methods such as sol–gel techniques.[31] In both cases, there is initial mixing of the reagents at the atomic level and a subsequent reaction between very finely sized particles.

Conclusions

It is possible to obtain in situ deposits of $YBa_2Cu_3O_{7-\delta}$ with bulk superconducting properties by simultaneous electrodeposition of its elements in DMSO over silver substrates, using cyanide as complexing agent for copper ions. The use of this complexing agent leads to similar reduction potentials for Y, Ba, and Cu and, therefore, to achieve the optimal conditions for co-deposition of the three elements that will be mixed at an atomic level. The identity of the complex formed in DMSO is not fully known, and further work is in progress. Potassium gets deposited together with the three metals that form the superconductor, but the thermal treatment eliminates it completely from the deposit. Its role in the kinetics of deposition appears to be notable and is being studied. The reaction among precursors under an oxidizing atmosphere shows reduced temperatures for the obtention of Y_2BaCuO_5 and $YBa_2Cu_3O_{7-\delta}$ similarly to other soft-chemistry methods. The amount of impurities present in the final deposit is very small compared with previously reported data on deposits obtained by electrodeposition. Furthermore, the physical properties, $T_c = 92$ K, and $J_c = 51$ A cm^{-2}, as well as superconducting fractions (60%) are improved with respect to the few reported previously on samples obtained by electrodeposition on metallic substrates. Two reasons may be responsible for that. First, the use of cyanide allows the co-deposition of highly reactive precursors that yield the superconducting oxide $YBa_2Cu_3O_{7-\delta}$ after an oxidizing thermal treatment at relatively low temperature. This fact allows the use of substrates of low melting point inert chemically with respect to the oxide. And second, a long crystallization period is allowed for the oxide crystals to grow at a moderate temperature that is higher than the temperature of formation.

Acknowledgment. This work has been financed by the MIDAS Program (CICYT-Red Eléctrica de España, Grants 92/1592 and 93/2331), and the Spanish Ministery of Education and Science (CICYT, Grant MAT 93-0240-C04-01).

CM940524W

---

[31] Barboux, P. In *Chemistry of Superconductors Materials*; Noyes Publications: Park Ridge, NJ, 1992; Chapter 7.