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10 July 1991 In reply refer to G.O. 71033

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Office of Naval Research
800 North Quincy Street
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Attention: Dr. Wallace A. Smith

Subject: Quarterly R&D Status Report No. 3
"Electrodeposition of High Temperature Superconductors"
For period 03/01/91 through 06/30/91
Contract No. N00014-90-C-0225
SC71033.QRDSR

PROGRAM SUMMARY

The overall objective of this project is to develop a process for direct electrodeposition of Y-Ba-Cu superconducting oxides from a molten salt at relatively low temperatures (300-550°C). The approach entails establishing a sequence of electrochemical steps for the layered deposition of the Y, Ba, Cu oxide species from a molten Na-K nitrate eutectic.

PROGRAM STATUS

In the previous quarter we reported the dissolution and passivation of Cu in the molten Na-K nitrate eutectic melt. This can be considered a major milestone with respect to the feasibility of HTSC deposition from the molten salt since Cu can be both injected as a soluble species or stabilized with an insoluble oxide film. In this quarter we have demonstrated the potential dependent deposition of a 2000 Å Y-Cu oxide film on Cu electrodes exposed to a molten salt solution containing approximately 0.05 M Yttrium. This marks the achievement of another important milestone toward direct electrodeposition of Y-Ba-Cu superconducting oxides from the molten nitrate salt. Characterization of the potential dependence for Ba, and the simultaneous adsorption of Y and Ba on Cu and Cu oxide-covered electrodes is currently in progress. Most of the samples have been processed and are awaiting analysis. The electrochemistry of Y in the Na-K nitrate has also been defined.

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ACCOMPLISHMENTS

We previously evaluated the electrochemistry of Cu and determined that it could be electrochemically injected into the melt and deposited as CuO Fig. 1 shows an XRD for the CuO film formed at 0 V on a rotating Pt electrode.

In this reporting period, the electrochemical behavior of Y in the molten nitrate has been characterized. The results show that Y, like Cu, can also be electrochemically injected as a soluble species in the melt. A Y foil electrode was found to be very electrochemically active throughout the entire region of stability of the melt as shown by the current vs voltage curves in Fig. 2. Hence the material can readily dissolve by anodic electrolysis in the melt for voltages above -1 V. Note that a relatively low cathodic current occurs for potentials from -1 V to -1.9 V since the overvoltage for the solvent breakdown (-1.4 V on Pt) is dramatically shifted to more negative potentials at the Y surface. The important conclusion to be made from these observations is that a potential region exists (between -1V and -1.9 V) for which Y is stable and the rate of electrochemical decomposition of the melt is slow.

The ability of Y to anodically dissolve in the melt has allowed electrochemical injection of Y ions into the melt by polarizing the Y foil to 0 V vs Ag/Ag^+. Accordingly, a melt equilibrated at 300^0 C was made approximately 0.05 M in Y by anodic dissolution of 99.9% Y foil. Flag-shaped OFHC Cu electrodes were equilibrated in this melt for 1 minute at open circuit and then polarized for 5 min each at a different potential. The sample was then removed from the melt with the potential still applied to the lead and subsequently analyzed for surface composition using Auger electron spectroscopy (AES). Fig. 3 shows a plot of the atom % of Y, Cu and O on these samples as a function of potential. As can be seen in Fig. 3, there is a strong potential dependence for the adsorption of Y on the Cu. Above +0.2 V, Y adsorbs giving an atom % of 10-30%. A maximum of 30 atom% Y appears at -0.2 V. An Y-rich oxide appears to compete with a Cu-rich oxide for the surface. Furthermore the oxides appear to be compounds as evidenced from the depth profile obtained by combined Ar ion etching and AES analysis, the results of which appear in Fig. 4. Note in Fig. 4 that the distribution of the respective atomic species appears to be more or less constant throughout the first 2000 A in the case of the sample processed at -0.2 V.

The formation of a 2000 Å surface film with a Cu :Y ratio determined by electrochemical polarization marks an important milestone toward electrochemical synthesis of films of the Y Ba Cu HTSC oxide.

PROBLEM AREAS

Fragility of the rotating disk electrode used as an analytical tool has slowed somewhat, but has not impeded progress .

Dist A. per telecon Ms. Debra Hughes
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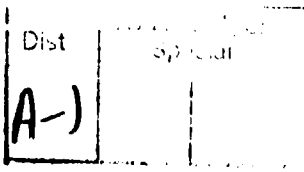

CORRECTIVE ACTION

Strict protocols on immersing and removing the rotating electrode from the hot melt so as to avoid thermal shock increases the mean time to failure of the electrodes.

GOALS FOR NEXT REPORTING PERIOD

We anticipate substantially achieving the following goals by the next reporting period:

Completed evaluation of the electrochemical dependent adsorption of Y on Cu electrodes as a function of electrochemical pretreatement in the molten nitrate.

Determination of the potential dependent adsorption and electrochemical behavior of Ba in the Na-K nitrate eutectic.

Deposition of Y, Ba, Cu oxide films on copper from a Na-K nitrate eutectic containing Y and Ba .

Determine conditions for which surface films having the Y Ba Cu stochiometry of the 123 HTSC oxide can be made.

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Martin W. Kendig for
D. M. Tench
Principal Investigator

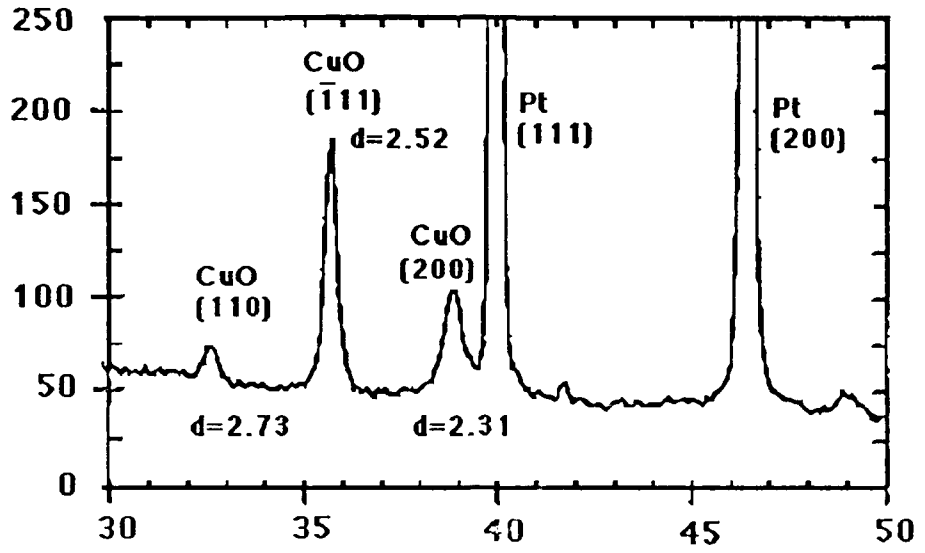

Fig. 1. X-ray diffraction for film formed on rotating Pt electrode (600 rpm) at 0 V for 70 min from a 300 ^{o} C Na-K nitrate eutectic melt containing electrochemically injected Cu(II) ions.

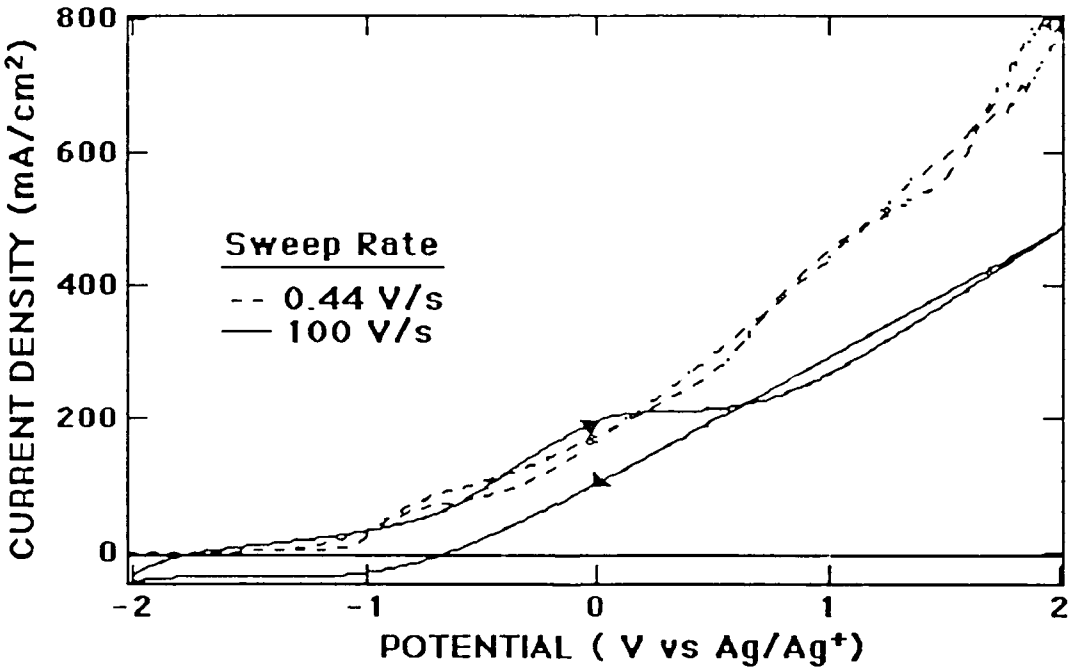

Fig. 2. Voltammograms for Y foil (99.9%) in 300^{o} C Na-K nitrate eutectic.

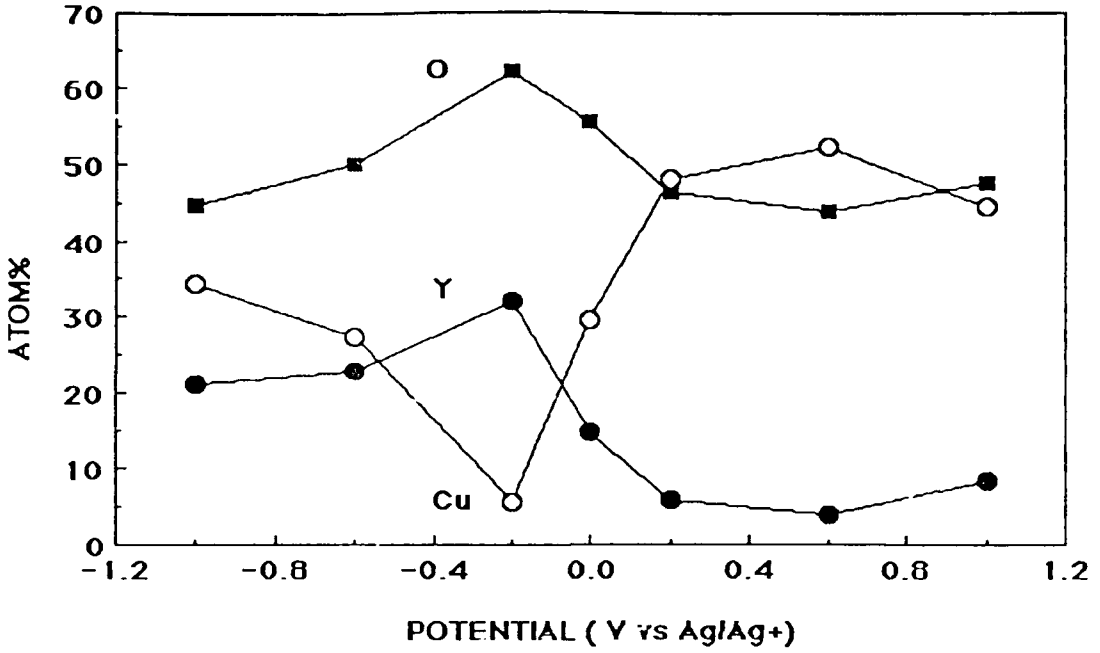

Fig. 3. Surface composition from Auger electron spectroscopic analysis of a film formed on OFHC Cu placed at open circuit for one minute in the 300^{o} C Na-K nitrate eutectic containing 0.05 M Yttrium and then electrochemically polarized to the potential of the abscissa for 5 minutes

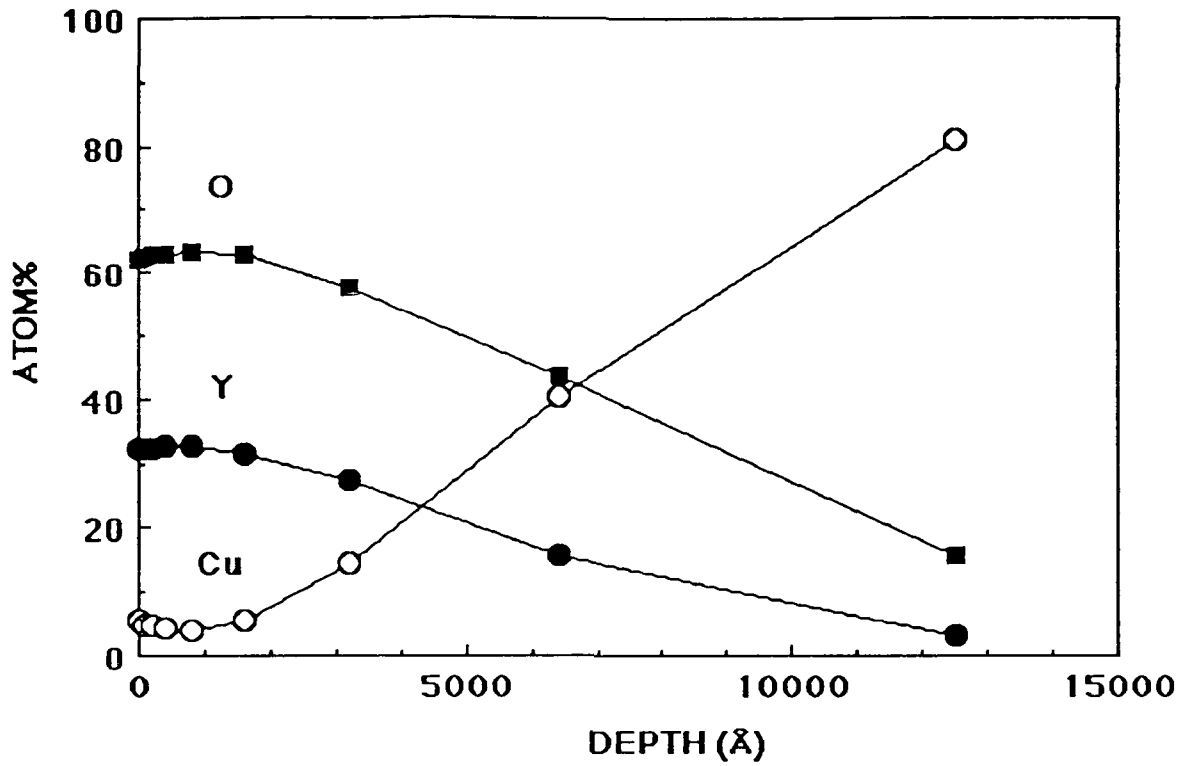

Fig. 4 Depth profile for the oxide on the sample processed at -0.2 V in the melt containing 0.05 M Yttrium

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