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Chemical and electrochemical oxidation of copper in dielectric millimeter waveguide tubes

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Chemical and electrochemical techniques are developed for oxidation of copper to constant thicknesses in 51 and 60 mm i.d. tubes up to 11 m in length. Comparison between these oxidation processes show the electrochemical process to be superior for this application. Differential double layer capacitance measurement of copper roughness after the oxidation indicates roughness factors between 3.2 and 9.9 depending on the thickness of the oxide. Potentiodynamic sweeps were used to investigate the mechanism of electrochemical oxidation in sodium hydroxide solutions saturated with copper containing complexes.

1. Introduction

Copper oxides have been studied as a bonding interface between copper and various dielectric materials [1, 2]. For specific applications [3, 4] the effects of the oxidation process on the surface roughness of copper may be critical [5–9]. Both chemical [1] and electrochemical [10–20] processes for oxidation of copper have been described extensively in the literature. Few studies are available for bonding of copper oxides to dielectric in tubes [1, 2] and the effect of the oxidation process on the surface roughness of copper. The purpose of this paper is to report on a study of chemical and electrochemical oxidation of copper in 51 and 60 mm i.d. tubes in lengths up to 11 m. It is also interesting to report studies of the effects of electrochemical oxidation of copper on the surface roughness of copper using differential double layer capacitance techniques.

2. Experimental procedure

The pretreatment of the copper, plated from a copper cyanide solution is the same for both the chemical and electrochemical processes. The pretreatment involved cleaning in an alkaline solution at 75–80° C for 10 min followed by rinsing with water then exposure to a 60 g dm^{-3} sodium cyanide solution at 25° C for 2–4 min. In both processes solution flow through the tube was 37.9–75.8 gal min^{-1} (172.3–344.6 dm^3 min^{-1}). After rinsing with water the copper was either chemically or electrochemically oxidized. Chemical oxidation consisted of recirculating the oxidizing solution through the tube back into the holding tank until the tube temperature reached 70° C. The solution was then allowed to remain static for 15 min after which solution flow was commenced until the tube maintained 70° C. The solution in the tube was then allowed to remain static for another 15 min. The temperature drop during each 15 min period did not exceed 5° C. The electrochemical oxidation technique required design and development of a special facility depicted in Fig. 1. The slender copper cathode, item 8, is kept stationary while the tube, or anode, item 4, is rotated by an electric motor connected to one of the sleeves into which the tube ends are clamped. Fig. 2 shows a section of the cell geometry. The Teflon member is helically wound around the internal copper cathode from one end of the tube to the other. Both ends of the spiral are held in the stationary components of the heads which also contain rotating sleeves for the rotation of the outer tube (anode). The 2 mol dm^{-3} sodium hydroxide solution used in the electrochemical oxidation process is presaturated by anodic polarization of copper at 7.1 mA cm^{-2} and 70° C. Fig. 3 shows the optical spectra obtained at

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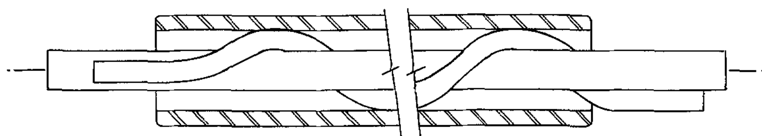

Fig. 1. Apparatus employed in the electrochemical experiments.

various pre-electrolysis times. During the electrochemical oxidation process the solution is stationary at 70–80° C and only the tube (anode) is rotating at 2 rpm. After the voltage (between the anode and cathode) increased, indicating oxygen evolution on the anode, the current was turned down to 1.75 mA cm^{-2} and the solution drained. The tube was rinsed and dried with air.

The procedure for analysis of the oxide thickness involves chronopotentiometric techniques in solutions of either 0.2 mol dm^{-3} NH_4Cl or 0.1 mol dm^{-3} KCl. In NH_4Cl solution two waves are observed and attributed to the cathodic reduction of Cu_2O and CuO. Only one reduction wave is observed in KCl solutions. Although it is known that copper oxides are not uniformly dense layers for comparison purpose, thickness is calculated on this basis. Fig. 4 shows the cell used for analysis of the oxide thickness for both the chemical and electrochemical processes. All thickness measurements were made at 1 mA cm^{-2}. The same cell design is used to determine variations of oxide thickness around the circumference by blocking off selected areas with a Teflon insert.

Differential double layer capacitance techniques [22] are used to determine the effect of the electrochemical oxidation process on the real surface area of copper. Both a rotating disc and tube electrodes were used in the study. The capacitance of the copper electrodes was determined in 0.8 mol dm^{-3} NaF [23] at a pH of 5.6–6.2. After electrochemical oxidation the oxide is stripped in 60 g dm^{-3} sodium cyanide at 25° C. The time of stripping depended on the thickness and composition of oxides but was usually in the order of 2–10 min. The capacitance was determined as a function of stripping time for each oxidation condition until both current–voltage and capacitance–voltage curves were at steady-state and showed no evidence of copper oxides present.

3. Results and discussion

Figure 5 shows thickness of Cu_2O and CuO versus tube length using chemical oxidation procedures. Also included are analyses of oxide thicknesses with repetitive use of the solution without replace-

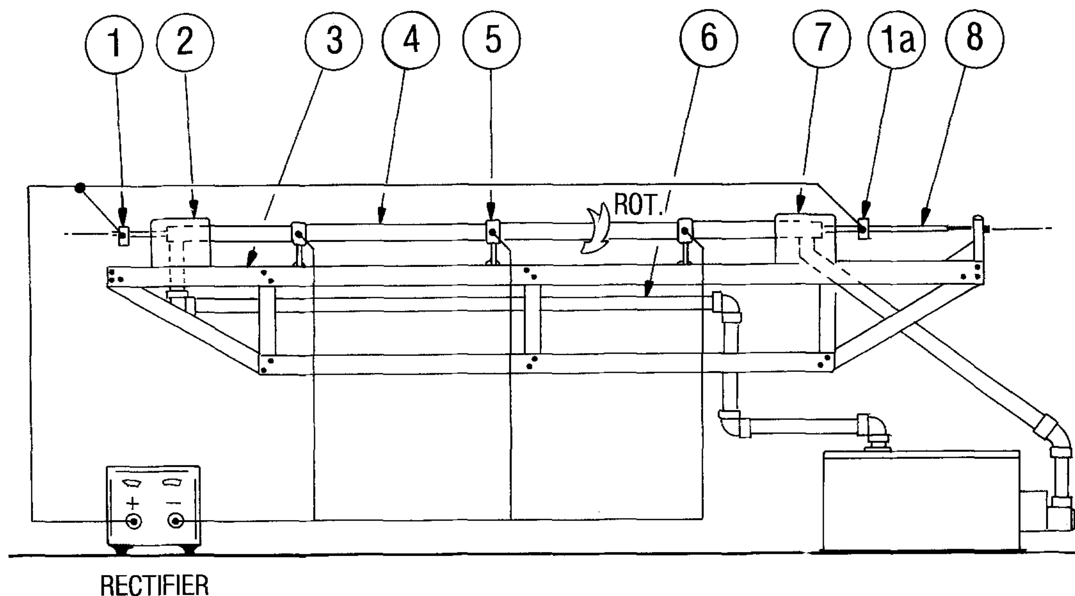

Fig. 2. Section showing cell geometry.

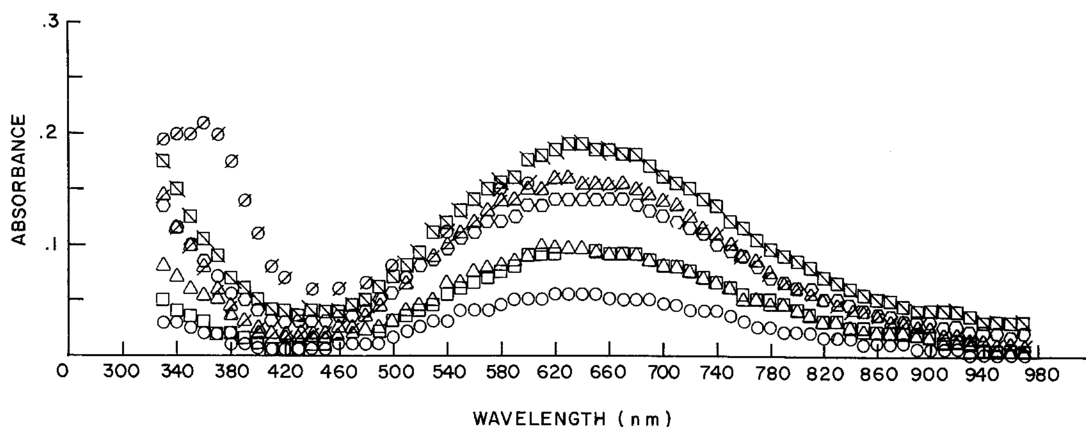

Fig. 3. Optical spectra of processing solution at various electrolysis times. Surface area/volume of solution, 4.48 X 10^{-2} cm^{-1}. Electrolysis times: ⌀, 31.5 h; ⌀, 26.5 h; ☆, 20 h; △, 14.5 h; □, 10.5 h; ○, 5.5 h.

ment of chemicals which had been depleted during the process. The thickness of Cu_2O appears to remain constant whereas the thickness of CuO decreases with solution usage. The coverage of copper with oxide also decreases with repetitive use of the chemical oxidizing solution as shown by scanning electron microscopy. Adhesion failures of these oxides bonded to polyethylene indicate cohesive failure within the oxide.

Figures 6 and 7 show thicknesses of Cu_2O and

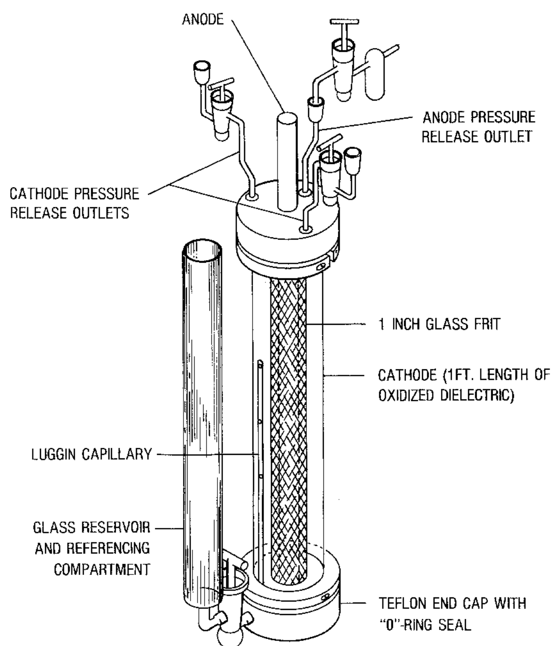

Fig. 4. Cell for chronopotentiometric analysis of oxide thickness.

CuO versus the tube length for various constant anodic current densities. Differences in values of oxide thickness between the 51 and 60 mm i.d. tubes in lengths up to 11 m are not statistically significant. More extensive studies at 7.1 $mA\,cm^{-2}$ illustrate thicknesses of both Cu_2O and CuO are independent of solution usage. Analysis of oxide thicknesses in both KCl and NH_4Cl solutions are shown in Table 2. Also shown for comparison are thicknesses expected from the voltage–time curves during growth of the copper oxide. When the voltage–time curves at constant current density are used, the following relationship is observed:

$$i\lambda^{1/2} = 0.102 \pm 0.010$$

where: i = current density; λ = transition time during growth of the oxide; 95% confidence levels, $6.88 \times 10^{-3} < \sigma < 1.83 \times 10^{-2}$; $0.0944 < i\lambda^{1/2} < 0.1095$. This relationship is valid for the current density range 3.5 to 18.5 $mA\,cm^{-2}$ in 2 $mol\,dm^{-3}$ NaOH at 70–80° C for tubes of 51 and 60 mm i.d. and lengths up to 11 m. A similar relationship has been previously observed [17].

Differential double layer capacitance–voltage curves are characteristic of those obtained by previous authors [22]. The roughness factor for mechanically roughened copper electrodes was constant between 0.2–0.6 V (SCE) for the test system chosen. The roughness factor after the first and second electrochemical oxidation processes are determined for a limited number of samples as a function of the number of coulombs passed per cm^2. Using a nonparametric statistical curve test including data for both the first and second oxida-

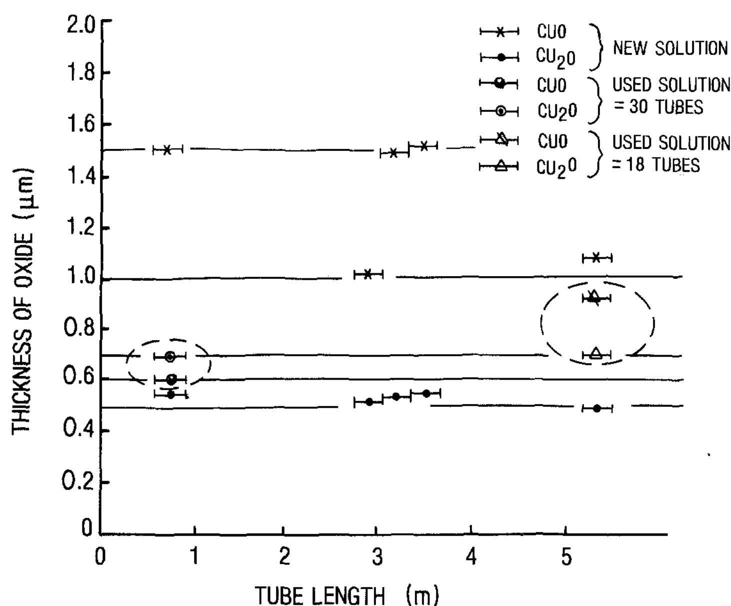

Fig. 5. Millimeter waveguide oxidation, chemical technique: Oxide thickness versus tube length and solution usage.

tion the hypothesis of no correlation between the roughness factor and the number of $C\,cm^{-2}$ is rejected at a 0.10 level of significance. Including only the first oxidation process in the analysis, the hypothesis of no correlation is rejected at a 0.02 level of significance. This analysis is limited to roughness factors between 3.2 and 9.9 and between 0.5–6.2 $C\,cm^{-2}$. The roughness factor does not increase continuously but decreases as the charge density reaches 52–55 $C\,cm^{-2}$.

Potentiodynamic sweeps for the anodic oxidation of copper and subsequent reduction of copper oxides formed in 2 mol dm^{-3} NaOH solutions saturated with copper ions show the characteristic peaks at 25, 30, 40, 60 and 80° C. Only on the anodic side of the reduction peaks for CuO

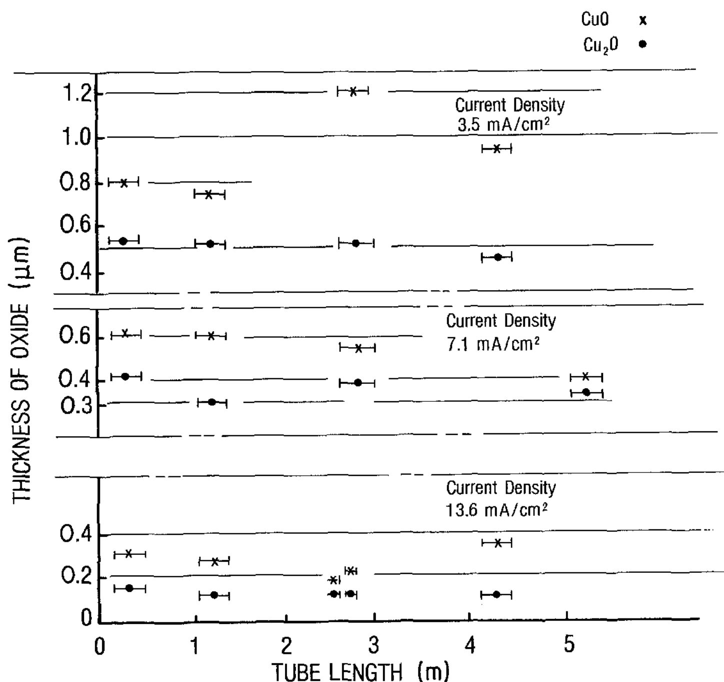

Fig. 6. Millimeter waveguide oxidation, electrochemical technique: Oxide thickness versus tube length and current density.

Table 1. Oxide thicknesses deposited by the chemical technique, measured at various areas of circumference (μm). *Tube 664*

Tube length (ft)†	*Arc of circumference*							
	30°		90°		180°		270°	
	Cu_2O	CuO	Cu_2O	CuO	Cu_2O	CuO	Cu_2O	CuO
11	0.593	1.44	0.533	1.56	–	–	–	–
10	0.623	1.47	0.464	1.94*	0.584	1.52	0.470	1.22

* May be considered high due to depolarization effects observed in the transients.
† 1 ft = 3.0480×10^{-1} m.

Table 2. Thickness of oxide deposited by the electrochemical technique (μm). *Measured at various positions along the tube*

Position in tube measured from entrance (in)‡	*0.2 mol dm^{-3} NH_4Cl separate transition*			*0.2 mol dm^{-3} NH_4Cl total transition*	*2.0 mol dm^{-3} NaOH* total transition for tube*	*0.1 mol dm^{-3} KCl total transition*
	Cu_2O	CuO	Total			
Tube 771						
49.5 to 54	0.674	0.773	1.45	1.13	–	–
108 to 112.5	0.674	0.809	1.48	1.16	1.46	1.09†
147.5 to 162	0.526	0.914	1.46	1.28	–	1.27†
Tube 774						
49.5 to 54	0.520	0.651	1.17	0.92	–	0.98†
103.5 to 108	0.539	0.590	1.13	0.87	1.33	1.13†
162 to 166.5	0.647	0.703	1.35	1.04	–	–

* Solution saturated with copper ions by anodic dissolution.
† Adjacent 4 inch section to samples in column 1.
‡ 1 in = 2.54 cm.

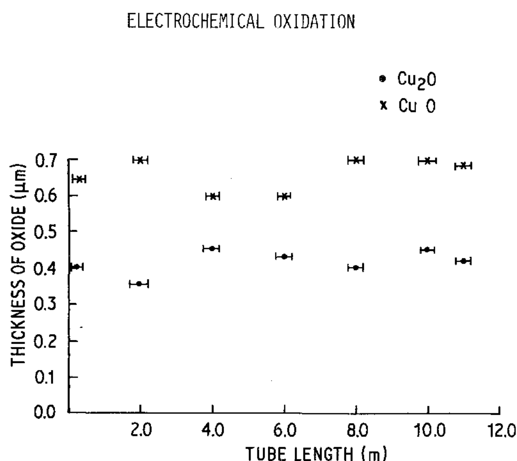

Fig. 7. Variation of oxide layer thickness with tube length.

at 60° C does there appear to be another resolvable peak. Plots of the anodic peak height versus the square root of the scan speed are similar to that observed in pure NaOH at 25° C. It appears that neither increased temperatures nor the presence of a saturated solution of copper containing complexes alter the mechanism of formation of either Cu_2O or CuO. Potentiodynamic sweeps on platinum in the 2 mol dm^{-3} solution saturated with copper containing complexes indicates at least three electroactive species due to Cu^{2+}, $HCuO_2^-$, CuO_2^{2-} [24].

A pilot plant was built using the electrochemical oxidation process as a basis for designing scaled up facilities. The reproducibility and reliability of the electrochemical oxidation process was shown

by producing over 2 miles of dielectric lined waveguides.

Acknowledgements

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