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SURFACE ANALYSIS OF CHROMATE TREATED COPPER

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ABSTRACT

The oxide layers of copper specimens formed by the commercial etching agent Isoprep 201 have been examined by the surface analytical techniques of ESCA spectra and Auger depth profiling. The result indicates that the agent has reduced significantly the surface oxidation, as well as the tarnishing effect of copper. The presence of Cr on the oxidized surface is found to play a major role in the oxidation kinetics at room temperature.

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INTRODUCTION

In the letter dated February 23, 1989, Rockwell International Company recommended the use of copper-chromate as a leading finish for all electronic components. Isoprep 201 manufactured by Allied-Kelite was suggested as a leading dip brightener.

To evaluate the effectiveness of Isoprep 201,* as well as the mechanism involved in the finish protection, Electron Spectroscopy for Chemical Analyses (ESCA) and Auger depth profile analyses were performed on 15 copper specimens that were treated with Isoprep 201 following the manufacturer's recommended procedure. The ESCA technique was used for the determination of the chemical composition, as well as chemical states of elements on the copper surfaces, and the Auger depth profile analyses for the measurement of the protective copper oxide layer thickness.

EXPERIMENTAL

Copper Specimens

Two different types of copper were used: high purity copper sheet stock and oxygen free copper (OFHC). The high purity copper sheet obtained from stock copper, as well as the oxygen free copper from high vacuum chamber gaskets, was about 2 mm in thickness. The OFHC copper has at least a 99.9% metal purity with less than 1% oxygen. The two samples were then cut into specimens approximately 1 cm by 1.5 cm in dimension. Eight specimens from the high purity copper stock (divided into two sets) and seven specimens from OFHC (one set) were prepared.

Chemical Treatment

Prior to dipping into the Isoprep 201 solution, the specimens were washed and rinsed in distilled water. The additional cleaning was made in the third set of seven specimens which were cleaned by Micro Laboratory cleaner in an ultrasonic bath. Handling of the specimens was made only with stainless steel tongs and tweezers to minimize contamination. The chemical solution containing a 1:1 ratio of Isoprep 201 (18.45% chromium compound, 4.3% nitric acid, and 2.8% sulfuric acid by weight) and distilled water was constantly agitated by a magnetic stirring rod while the specimen was immersed for a given time period. After dipping, the surface of the specimen was carefully cleaned and rinsed and distilled water at least three times to remove the remaining etch solution; then, the specimens were thoroughly dried and placed in a dessicator overnight. The oxidation of the specimens was performed in an oven heated at $75^{o}C \pm 5^{o}C$ for 24 hours. Immediately after the oxidation, the specimens were mounted and placed into the vacuum chamber of the ESCA/Auger instrument to minimize hydrocarbon film formation.

Three sets of specimens were prepared: the first and second sets each contained four specimens, and the third set contained seven specimens. The first set of four specimens prepared from copper sheet stock (designated as CP), had dip times of 15, 30, 60, or 120 seconds in the 1:1 solution at room temperature. These four specimens were coded with "D" according to the length of the dipped time ranging from 15 seconds to 120 seconds. Thus, the specimens were designated as D1, D2, D3, and D4 according to the dipping times of 15, 30, 60, and 120 seconds.

*Isoprep 201, the etch solution contains chromate and other acids made by Allied-Kelite Division, Witco Chemical Co., Des Plaines, IL 60018.

The second set of four specimens prepared from the same copper sheet stock had similar dipping times to the first set except the etching was performed at $40^{o}C \pm 2^{o}C$. They were coded similarly to the first set with "E". Thus, the four specimens were designated as E1, E2, E3, and E4 according to the dipping times of 15, 30, 60, and 120 seconds.

The seven specimens made from OFHC (designated as CU) were prepared at room temperature having varying dip times from 0 seconds to 60 seconds at an interval of 10 seconds. After dipping, the specimens were oxidized at $75^{o}C$ in an oven under ambient atmospheric convection for a period of 24 hours. The designations of these oxidized specimens are CU00 to CU60.

Instruments and Procedure

ESCA Surface Composition Analysis

The analysis was performed in the ESCA/Auger instrument, PHI Model 548, made by Physical Electronic Ind., Inc. The objectives were to identify the chemical constituents of surface elements, to determine the atomic surface concentrations, and to examine probable chemical binding states of the elements.

First, a survey spectrum (0 eV through 1000 eV) was taken to identify all elements present on the surface. The identities of the elements were established from the binding energies of observed peaks on the spectra. Afterward, a detailed scan spectrum (20 eV width) with a higher resolution and sensitivity was obtained for each element identified in the survey spectrum. The narrow scan spectra produced the precise binding energy of the atomic element which could be used to determine the magnitude of the so-called chemical shift. From the binding energy shift, the chemical binding state of the element could be determined.

The integration of the peak yields the abundance of the element present on the surface. The surface atomic concentration is calculated from the integration of all peak areas after the atomic sensitivity calibration.[1] The peak lineshape also provides information concerning the variety of different binding states of an element present on the surface.

Auger Depth Profile Analysis

Auger electron spectroscopy, together with ion beam sputtering, is used to determine the thickness of the oxide layers formed on the etched specimen surfaces. The peak position of the element is first established by Auger wide spectra, then the peak magnitude of the element is monitored while the surface layer is sputtered by the argon ion beam. The depth of the surface oxide layer is determined from the time required to reduce the oxygen peak amplitude or to reach a steady state copper concentration. In the present study, the sputtering is provided from a static argon pressure of 5×10^{-5} torr at 5 kV, and the surface removal rate is calibrated against a known thickness of silicon oxide film 120 Angstrom (Å). The time required to etch away the silicon oxide layer is then converted into the sputtering rate for the oxide layer on the copper specimens. The sputtering rate may yield an error of 25% to the calculated layer thickness.

1. BRIGGS, D., and SEAH, M. P. *Practical Surface Analysis*. John Wiley & Sons, New York, NY, 1984.

RESULTS

ESCA Analyses

From ESCA spectra, elements such as carbon, copper, oxygen, and sulfur were identified in all specimens. Chlorine and chromium were present in a few, but not all, specimens. Due to the sensitivity limit of the present instrument, an element with the concentration less than 1% was not detected. In Figures 1a through 1c, the atomic concentrations with varying dipping times are shown for these three sets of specimens. For the oxidized surfaces (CU00 through CU60) in Figure 1a, copper, carbon, and oxygen in order of decreasing abundance are dominant elements on the surface followed by a few percent of sulfur and chlorine. It is important to emphasize that no chromium is observed after oxidation.

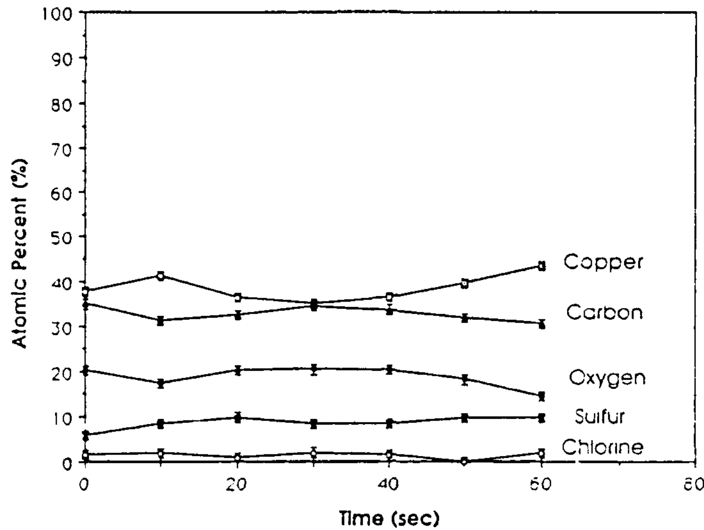

Figure 1a. Surface concentrations of elements observed in copper specimens after Isoprep 201 solution treatment. Oxygen free copper specimens, dipped at room temperature and followed by oxidation at 75°C for 24 hours.

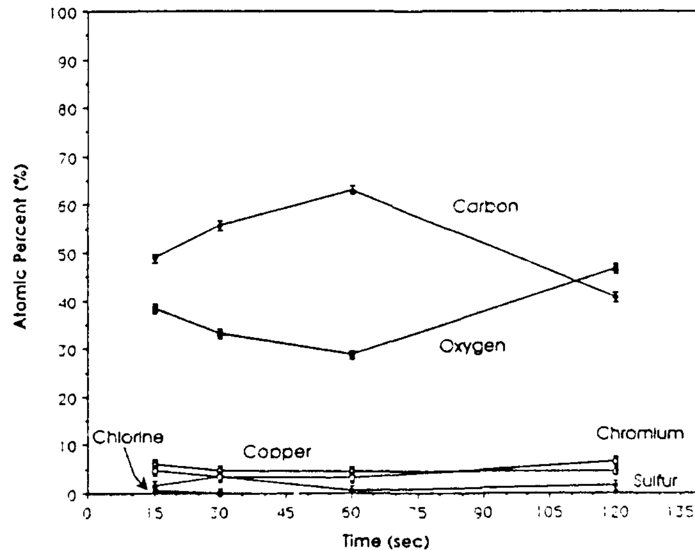

Figure 1b. Surface concentrations of elements observed in copper specimens after Isoprep 201 solution treatment. Copper sheet specimens dipped at room temperature.

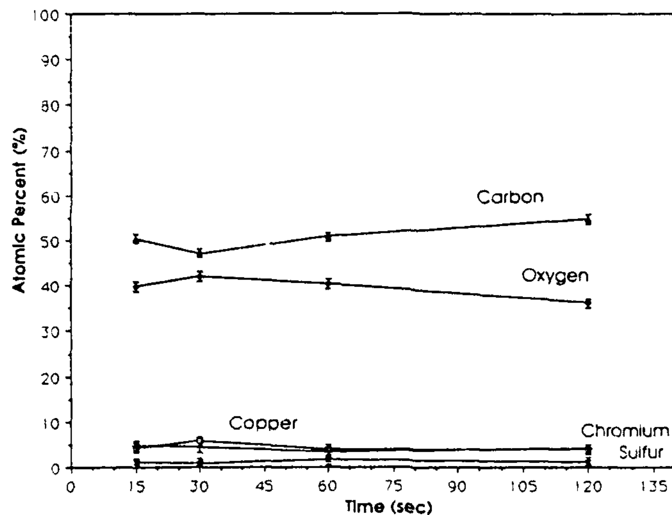

Figure 1c. Surface concentrations of elements observed in copper specimens after Isoprep 201 solution treatment. Copper sheet specimens dipped at 40°C bath.

In the dipped but not oxidized surfaces (CPD and CPE specimens) shown in Figures 1b and 1c, carbon followed by oxygen, is the major surface element; small amounts of chromium, copper, sulfur, and chlorine are also present. Chromium, a major constituent of the etch solution, is not present as a dominant surface element. The concentrations of Cu and Cr are roughly the same in the range of a few atomic percent.

The chemical binding states of these surface elements are described as follows:

Copper – The 2P 3/2 peak of Cu metal occurs at the binding energy of 932.4 eV, that of CuO at 933.6 eV, and $CuSO_4/Cu(NO_3)_2$ at about 935 eV. The present analysis clearly indicates that there are two overlapping peaks at the Cu 2P position. These two peaks are identified as Cu metal at 932 eV and Cu^{++} at 935 eV (such as copper sulfate and nitrate). The intensity ratio $Cu:Cu^{++}$ varies from one (equal proportion) to less than two. A small amount of CuO (933 eV) might also be present and was hard to separate and identify from the overlapping peak.

Oxygen – The binding energy of oxygen coming from Cu_2O and CuO is listed at 530 + 0.5 eV. In the specimens CPD and CPE series, the oxygen peak centers around 531 eV with a wide peak width. This broad peak profile strongly suggests that oxygen comes, not only from metal oxides, but also from other oxygen containing compounds such as sulfate (532 eV), hydroxide (531.5), and organic ketone/acid. Since no bump or shoulder is clearly visible from the oxygen peak profile, the exact binding state of oxygen is difficult to establish. In the specimens after oxidization (CU00 through CU60) at 75°C, two overlapping peaks with varying proportions are clearly visible. Both peaks are assigned tentatively to CuO and $Cu(OH)_2$.

Carbon – The carbon 1S peak usually consists of an asymmetric peak with the extended shoulder at higher binding energies. The shoulder is attributed to the existences of hydroxyl, carbonyl, and carboxyl groups in the hydrocarbon chains. The source of carbon in such a large quantity observed on the dipped surfaces is not clear. It might be derived from hydrocarbon contamination and might also come from the unknown organic chromate compound in the dip solution.

Chromium – The Cr 2P peak is observed in the dipped surfaces but not in the oxidized specimens. The binding energy of Cr is 576.8 + 0.2 eV, which indicates that Cr is present as CrOOH and Cr_2O_3. The peak shape of this low abundant element is fairly symmetric.

Sulfur – The sulfur 2P peak is observed at 168.2 + 0.2 eV for the dipped surfaces and is detected at 162.1 + 0.2 eV for the oxidized specimens. From the binding energies of sulfur, the element is found to exist as sulfate in the dipped surfaces and as metal sulfide in the oxidized specimens. The sulfur is largely derived from sulfuric acid in the dipped solution, but the process involving the chemical reaction from sulfate to sulfide upon oxidation is not clear.

Chlorine – The element is observed on the oxidized OFHC specimens after the treatment with the Micro Laboratory cleaning agent. The binding state of Cl 2P is 199.9 + 0.1 eV which corresponds to metal chloride. The source of Cl is not clear; it could be either a contaminant or a component of the solution.

Specimens CU00 Through CU60

In the oxidized specimens copper, sulfur, oxygen, carbon, and chlorine were observed on the top surface. Chromium was not detected. The absence of chromium suggests that Cr might have diffused inward during the oxidation but the concentration is probably below the level for detection. The information derivable from the binding energy data indicates that copper was found to be copper oxide and sulfide. Carbon is identified as hydrocarbons and chlorine as copper (II) chloride. Chlorine is probably a contamination from the cleaning agent used in the sample preparation. However, the element might be derived from the left-over of the etch solution.

The surface concentration of each element is shown in Figure 1a. Copper has the highest concentration followed by carbon, oxygen, sulfur, and chlorine. The concentration was as follows: copper about 45%, carbon 35%, oxygen 20%, sulfur 7%, and chlorine 1%. The variation of the surface composition is found to be minimal with dipping times.

Specimens CPD1 Through CPD4

In these specimens copper, sulfur, oxygen, carbon, and chromium were observed except a small amount of chlorine is detected in the CPD1 specimen. From the binding energies of these elements the top surface layer probably consisted of copper, chromium oxides, and sulfates. Chlorine exists as metal chloride probably as copper (II) chloride. Carbon could derive either from hydrocarbons contamination or from the Isoprep etch solution.

The atomic surface concentrations of these elements are shown in Figure 1b. The carbon and oxygen concentrations are around 50% with carbon slightly higher. The abundance of carbon tends to rise steadily with the dipping time and then drops at the specimen D4. The oxygen concentration decreases with increasing dipping times. The concentrations of copper, chromium, and sulfur, less than 10 atomic percent, are fairly the same regardless of the dipping times.

Specimens CPE1 Through CPE4

In these specimens dipped at the 40°C temperature bath copper, sulfur, oxygen, carbon, and chromium are observed. No chlorine was detected. From the observed binding energy data, copper and chromium were present as oxides and sulfates. Carbon probably comes from hydrocarbons derived either from surface contamination or from a constituent of the Isoprep 201 solution. The surface concentrations are shown in Figure 1c. Both carbon and oxygen concentrations are around 50% with carbon slightly higher. The three elements of copper, chromium, and sulfur were below 10 atomic percent. The surface abundances of these five elements changes little with the dipping time.

Auger Depth Profile Analysis

The oxide layers formed on the surfaces of all dipped specimens are determined by Auger depth profile analyses. The results are summarized in Figure 2. Three curves are shown, one for each set. The specimens oxidized for 24 hours (CU00 through CU60) have the thickest copper oxide layers (ca. 880 Å), which gradually increase with the dipping times. The specimens dipped at room temperature (CPD1 through CPD4) have thicker layers of copper oxide (approximately 175 Å) than the specimens (CPE1 through CPE4) dipped at 40°C (ca. 100 Å).

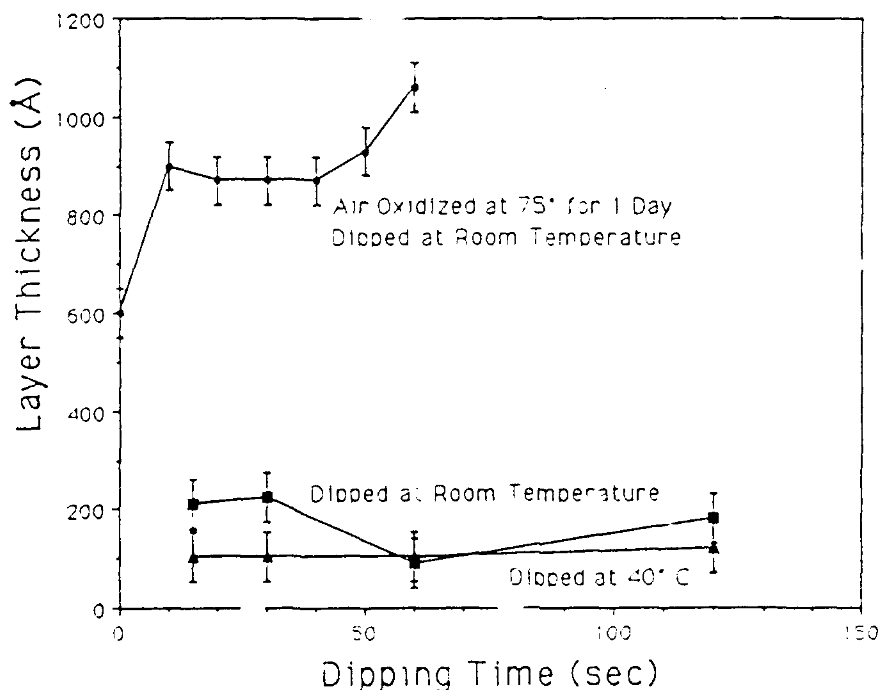

Figure 2. Thickness of copper oxide layer after dipping in Isoprep 201 solution.

The sputtering rate was calibrated from a known thickness of silica film on silicon. The depth of the oxide layer is calculated from the time required to reach a steady state signal from the sputtering onset, and the required time is then converted to the layer thickness in Å by the calibration. Due to the unknown surface nature of the copper oxide layer, as well as the sputtering behavior of silica, the layer thickness might be subjected to a high uncertainty of ± 25% plus an additional error resulting from the instrumental measurement.

In Figure 3 a typical depth profile analysis is shown: the peak magnitudes of elements vary with sputtering time. The surface of the specimen (CU50) was sputtered at an argon static pressure of 5 x 10⁻ torr, and the calibrated sputtering rate was 300 Å per minute. Five depth profiles are shown: sulfur, copper, oxygen, carbon, and nitrogen. Prior to the ion sputtering, all elements have essentially steady amplitudes. As the sputtering progresses, the signals of sulfur, carbon, and oxygen decrease while the signal of copper increases. The magnitude of nitrogen stays the same. The sharp intensity drops in the carbon and sulfur profiles indicates that the elements exist only on the top surface layer. Moreover, the oxygen signal increases abruptly at the onset of the sputtering and then decreases slowly. The gradual tapering of the oxygen amplitude shows that a concentration gradient might exist along the layer depth. The copper concentration always increases with the sputtering time.

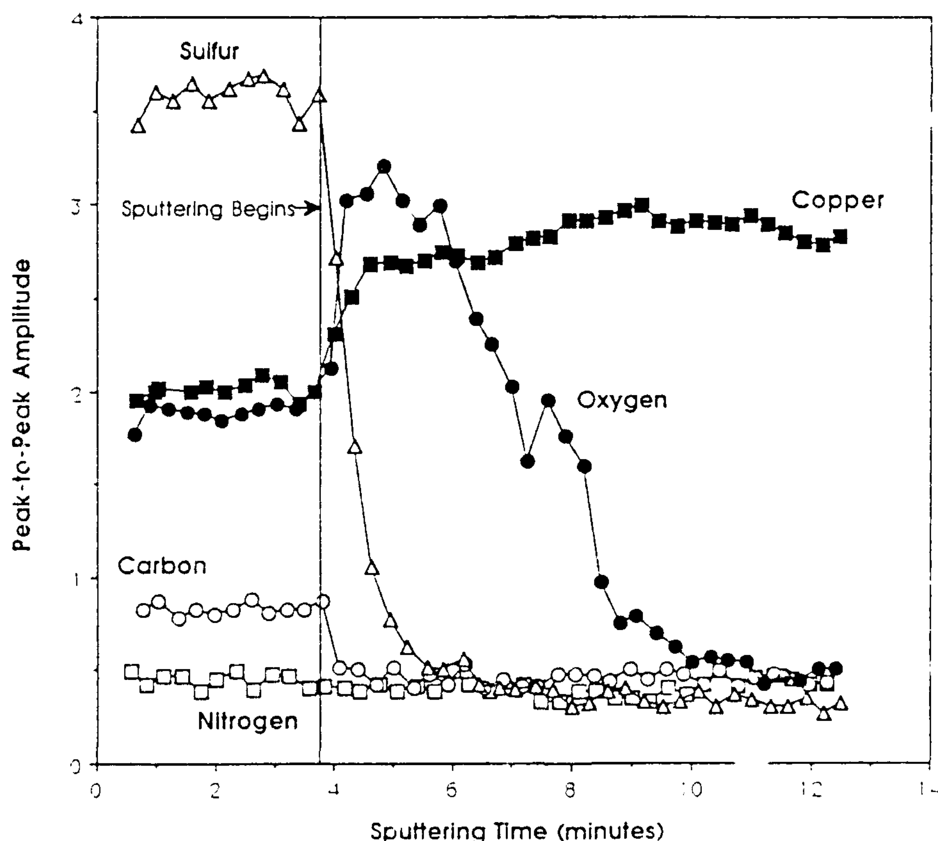

Figure 3. Depth profiles of copper oxide film.

From the depth profile analyses, sulfur and carbon are present only on the top few surface layers but not more than five atomic layers. Oxygen is believed to have a concentration gradient along the oxide layers as does copper. Chromium was observed neither on the surface nor at the subsurface layers. Nitrogen, a constituent of the etch solution, was not observed.

Additional information concerning the elemental distribution is also obtained from a few scanning Auger microscopic (SAM) images. The lateral distribution of the elements could be used to support the observation from the ESCA binding energy information. As shown on the SAM images in Figure 4, oxygen and sulfur are clustered on the same areas indicating the formation of sulfate compounds. A few spots of highly concentrated carbon are randomly dotted in this same area. Copper (not shown) is found to locate away from the high density area of the sulfate image.

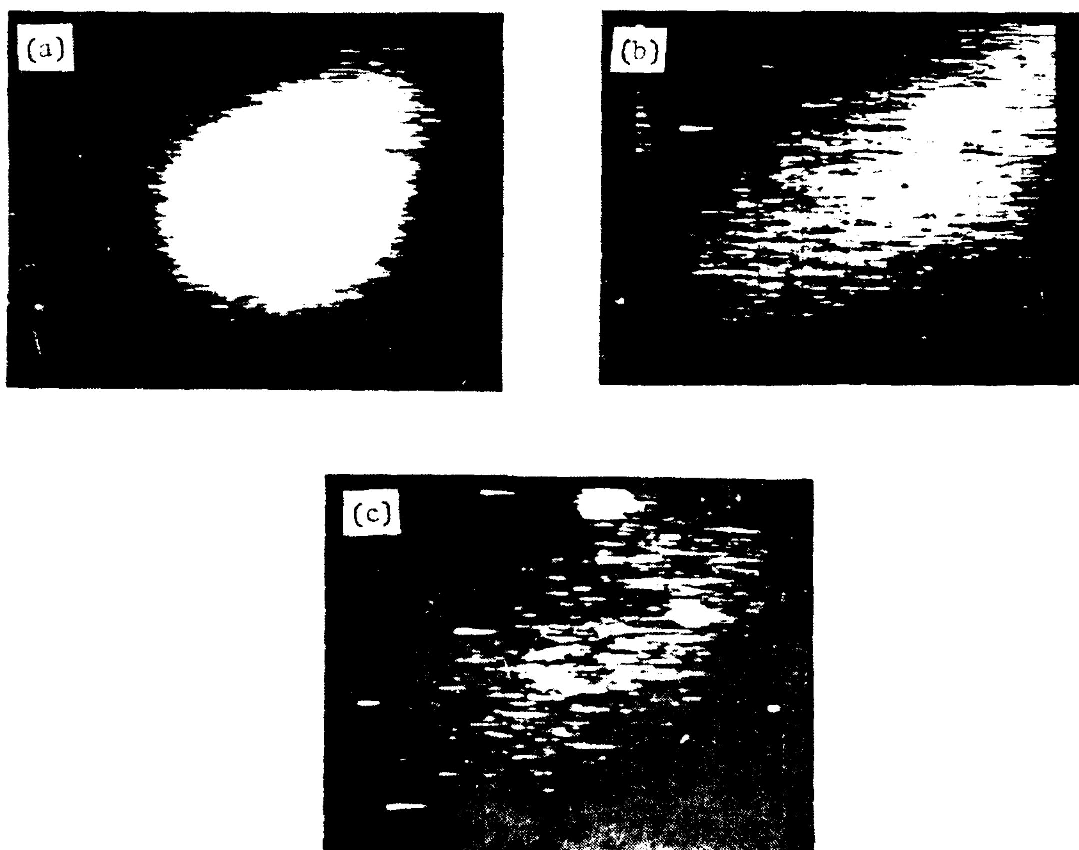

Figure 4. Scanning Auger microscopic images of copper oxide film specimen CPE1xx at 40°C for 15 seconds:

(a) oxygen (frame width 2 mm)
(b) sulfur
(c) carbon.

DISCUSSIONS

Isoprep 201, a dip brightener for copper alloys, claims to remove tarnish and corrosion deposits from parts made of copper alloys. The brightener also provides long term tarnish and corrosion protection by formation of an invisible film on the metal surface.

The dip solution contains 4.3% nitric, 2.8% sulfuric acids, and 18.45% chromium compound by weight. The ingredients of the chromium compound are not known (proprietary information). It is highly possible that the chromium compound includes chromic acid, potassium per chromate, and some organic chromates. Tests performed in several manufacturing sites have confirmed that the solution has indeed protected the brightness of copper alloys. The exact mechanism involved in the protection mechanism is not clear at this time. From the present surface analyses, a probable mechanism is proposed.

Extensive surveys concerning the oxidation of copper have been made.[2,3,4] Copper has been found to oxidize according to the inverse logarithmic and direct logarithmic relationships around 150°C. Above about 200°C up to 1000°C the oxidation of copper is essentially parabolic and the cubic law appears to be applicable at intermediate temperatures. The cubic relation may be considered as a deviation from parabolic oxidation owing to secondary effects such as cracking, changes in orientation in the scale,[4] delays in the conversion of Cu_2O to CuO_2, or aging of the scale.

The oxide film formation on the copper metal surface at room temperature is known to follow a logarithmic relationship in which the transport of cations Cu^+ determines the rate of oxidation. According to the mechanism suggested by Cabrera & Mott,[2] a chemisorbed oxide film exists on the metal and ions and electrons move freely in the film. At low temperatures the ions cannot simply diffuse through the film from a concentration gradient of ions, but the electrons are supposed to be able to pass from the metal to the oxygen absorbed on the surface of film either by thermo-ionic emission or, more probably, by the tunnel effect. In this case, cations are formed at the metal-oxide interface and oxygen anions at the oxide-gas interface. Thus, a strong electric field would exist across the oxide film which would be mainly responsible for pulling the ions through the film.

In the room temperature oxidation, electrons penetrate the thin oxide film by the tunnel effect leaving the equivalent number of metal ions behind. The electrons also transform the oxygen absorbed at the surface into $O^=$ ions and, therefore, set up an electric field across the layer. A state of quasi-equilibrium will be obtained in which metal ions diffuse. Thus, this strong field could enforce a directional movement of cations across the film at temperatures where normal diffusion is too small to be accomplished. Thus, the oxidation rate is dependent upon the number of excess atoms of oxygen at the surface, field strength, and defects on the oxide layer.

The tarnished appearance of oxidized copper is caused by the electron deficiency in the thin oxide layer of the Cu-Cu_2O-O_2 system. The number of cation holes per cubic cm is proportional to the number of oxygen atoms at the surface. The brightening action of Isoprep

2. CABRERA, N., and MOTT, N. F. Rep. Progr. Phys., v. 12, 1948, p. 163.
3. TYLECOTE, R. F. J. Inst. Met., v. 78, 1950, p. 259.
4. RONNQUIST, A., and FISCHMEISTER, H. J. Inst. Met., v. 89, 1965, p. 65.

201 seemed to decrease either the number of cation holes or the number of surface oxygen atoms which leads to a low rate of oxidation at room temperature.

From the present results, the possible cations from the Isoprep 201 solution are Cr^{+++}, H^{+}, and Cu^{++}. Since Cr is not observed on the oxidized surfaces but on the dipped ones, it is likely that the element has decreased the number of cation holes. Absence of Cr in the oxidized surfaces showed that no protection occurred which indicated that Cr played a major role in preventing room temperature oxidation, as well as in diminishing tarnish effect.

The presence of a large amount of SO_4= on the surfaces also indicates that the number of available oxygen atoms on the oxide-gas interface is decreased. Consequently, the strength of the electric field is reduced which could result in a slower oxidation rate. The carbon film, probably hydrocarbon, on the layer surface is also believed to reduce the number of available oxygen anion sites.

CONCLUSION

The present surface analyses supported the fact that Cr^{+++}, $SO_4^{=}$, and hydrocarbon derived from the Isoprep 201 solution on the thin copper oxide film could have reduced the oxidation rate at room temperature, as well as the tarnishing effect of the copper surfaces at ambient atmosphere and temperature. The diminishing rate of the oxide layer formation is attributed to the decreasing number of cation holes in the thin oxygen layer. Due to the presences of Cr^{+++}, $SO_4^{=}$, and hydrocarbon on the treated surfaces the number of available sites for oxygen absorption is reduced. The diffusion of cation Cu^{++} from the metal-oxide interface is also retarded owing to a lower strength of electric field existing across the oxide layer.

The present observation is consistent with the proposed mechanism[2] of the logarithmic oxidation rate of copper at room temperature. The blocking effect of Cr in the formation of cation holes plays a major role in the room temperature oxidation kinetics.

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The oxide layers of copper specimens formed by the commercial etching agent Isoprep 201 have been examined by the surface analytical techniques of ESCA spectra and Auger depth profiling. The result indicates that the agent has reduced significantly the surface oxidation, as well as the tarnishing effect of copper. The presence of Cr on the oxidized surface is found to play a major role in the oxidation kinetics at room temperature.

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