Colored Conversion Films of Mo-S-Cu Cluster Compounds on a Copper Surface

By X.R. Ye, X.Q. Xin and H.N. Zhou

Conversion films of Mo-S-Cu cluster compounds with a metallic luster of various colors have been obtained on a copper surface; their colors have been changed by heat treatment. Accelerated corrosion and tarnish tests indicate that PMTA passivation enhances the anticorrosive ability of the conversion films and the stability of their colors. FT-IR, XPS and AES determinations were made to investigate these conversion films before and after being heated. The results show that the colors of the heated and unheated films are probably caused by Mo-S-Cu bonds and a statistical distribution and overlapping of various molecular layers inasmuch as the films are complicated multicomponent and multilayer systems. The disparity of colors before and after heating treatment is caused by change of composition and structure of the films.

The coloring of metal is at present one of the interesting and important research fields of metal finishing. Metals are usually colored by chemical, electrochemical or heating treatment. Copper and its alloys are colored mainly by chemical or electrochemical methods, especially by chemical methods, to form conversion films of various colors. The films are functional finishing layers, possessing not only decorative properties, but improving the brightness and cleanliness of the metal surface, and promoting the anticorrosive ability of the metals as well. Accordingly, a great deal of research on the coloring of copper and its alloys has been performed.[1–5] To date, the primary coloring methods for copper and its alloys are oxidation or sulfidation by immersion in coloring solutions.[6–12] The following compounds are often used to make up a chemical oxidation or sulfidation solution for copper and its alloys: $NH_3 \cdot H_2O$, Na_2S, K_2S, ammonium polysulfide, persulfate (usually ammonium persulfate), NaOH, $KMnO_4$, molybdates (usually ammonium molybdate), ammonium sulfate, nitrate, the salts of copper or nickel, etc. Conversion films of the following colors can be obtained:

Fig. 1—Representative Auger electron spectra of unheated conversion film: (a) before sputtering; (b) after 2 min sputtering.

black, blue-black, blue-ashen, bright brown, dark brown, green, antique copper with golden yellow, antique copper, etc. For electrochemical coloring of copper and copper alloys, anodic oxidation is generally employed.[11,13] For example, black conversion films can be obtained from the anodic oxidation of copper in alkalized ammonium molybdate bath. Films of various colors can also be obtained, however, by electrolytic coloring of Cu, resulting from cathodic reduction of Cu_2O;[14] the films are bright, uniform, anticorrosive and wear-resistant. Their colors change from yellowish, golden or orange yellow, to pink to grass green with the reaction times. Further, a vapor reaction process has been developed for the antique green coloring of copper alloys.[15] Classifying by the composition of the colored films, we are able to draw the following conclusion: Cu_2O films are generally yellow, orange-yellow, red, purple and brown; CuO films are usually brown, black and cyan; CuS films display colors ranging from light brown to dark brown and ashen to cyan-black, while the films composed of alkaline substances are various greens. We can also find that the sulfur-containing compounds play an important role in the coloring of copper and its alloys. In addition to the sulfur-containing compounds, solutions containing inorganic selenium compounds,[16] (*e.g.*, K, Na or ammonium selenosulfide, $Me_2Se_2S_{2n}$, where n = 1 or 2) or a mixture of these compounds and solutions of thioantimonite Me_3SbS_3 are used for electroless coloring of copper and its alloys.[11] Both MoS_4^{-2} and WS_4^{-2}, the characteristics and reactivities of which, in the liquid and solid states, have been widely studied,[17–19] usually act as ligands in Mo(W)-S-Cu cluster compounds.[20–24] More than 160 cluster compounds with various framework structures have been synthesized by the reaction of these ligands with Cu^+.[25] Little investigation has been made, however, of their character and reactivities on a copper surface. We have studied the interaction between MoS_4^{-2}, or WS_4^{-2}, and
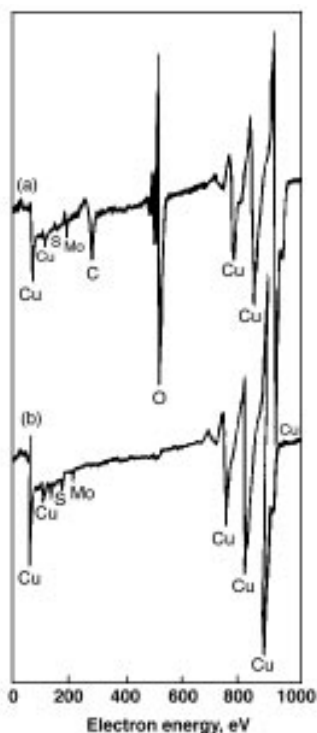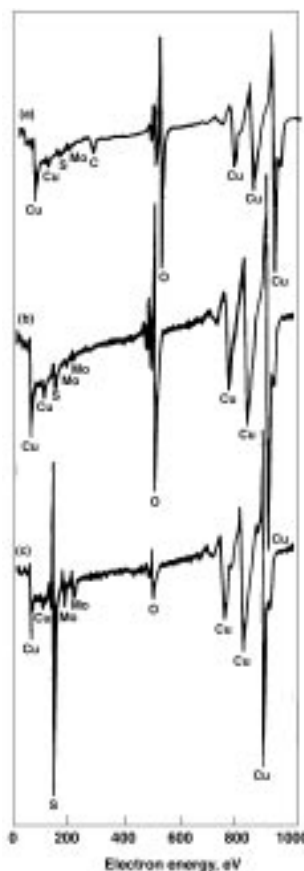

Fig. 2—AES of heated conversion film: (a) before sputtering; (b) after 6 min sputtering; (c) after 22.5 min sputtering.

Table 1

Table 1
Variation Sequence of Colors of Conversion Films

Reaction time, min	Color of unheated film	Color Sequence Heated in air 100 °C, 5–400 min
Mo-S-Cu film		
5	Brown	→Rose red→dark rose red→rose purple→blue→soft cyan →white
20	Rose	→ Blue → soft cyan → white
30	Blue	→ Soft cyan → white → light yellow
45	Soft cyan	→ White → yellow
60	White	→ Light yellow → yellow brown
W-S-Cu film		
2	Orange	→ Orange red → soft cyan → silver white → golden yellow
30	Orange red	→ Silver white → golden yellow→rose pink
50	Rose	→ Silver white → golden yellow
480	Silver white	→ Golden yellow
1080	Golden yellow	→ Brown

a copper surface, and have found the formation of insoluble cluster compound films of metallic luster and various colors changing with reaction times. Further, the colors of the films change gradually with heat treatment. These results are listed in Table 1. The known Mo(W)-S-Cu cluster compounds are usually dark red or orange, however, and their solutions are red or orange-yellow.[26-29] In this paper, the anticorrosive characteristics of the Mo-S-Cu conversion films before and after passivation are compared. The composition and structure of the films before and after heating treatment are discussed according to FT-IR, XPS and AES analysis, and the structures of the passivated films are also reported.

Experimental Procedure

Copper specimens were polished with MgO powder, degreased and dipped in dilute H_2SO_4 solution and washed in deionized water. After electropolishing in H_3PO_4 solution and rinsing with deionized water, the copper plates were immersed in 0.002 M of $(NH_4)_2MoS_4$ solution at 25 °C for different times, washed again with deionized water and dried with a cold air blast. As shown in Table 1, conversion films of various colors were obtained on the copper surface. Then the films were heated at 100 °C in air for 5 to 400 min; the variation sequence of their colors is also given in Table 1. The conversion films were passivated by immersion in 0.005 M of PMTA (1-phenyl-5-mercaptotetrazole) solution at 25 °C for 30 min, then rinsed with deionized water and dried by a cold air blast.

The accelerated corrosion test was performed by dipping the specimens in 10-percent NaCl solution at room temperature. The time at which the solution turned muddy was recorded, along with the extent of corrosion attack.
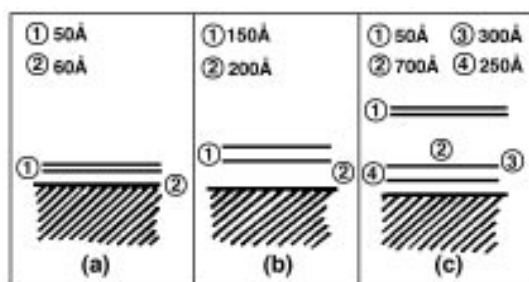

Fig. 3—Representative structure schemes of the heated and unheated films: (a) unheated brown film; (b) unheated white film; (c) white film resulting from heat treatment of the blue film at 100 °C for 10 min.

The accelerated tarnish test was carried out at room temperature in a glass vacuum desiccator, in which the concentration of H_2S was one percent. The tarnish time of the specimens was measured and recorded.

An FT-IR spectrometer was used to determine the reflection and transmission spectra (resolving power 4 cm^{-1}). An electron spectrometer with a magnesium X-ray anode (the energy of Mg Kα is 1253.6 eV) was used for measurements. Survey and high resolution spectra were obtained with the energy analyzer operating in a constant analyzer transmission energy mode at pass energies of 50 and 25 eV, respectively. The pressure in the analyzer chamber was maintained at less than 10^{-7} Pa during the analysis. The voltage and current of the electron beam for AES analysis were 3 kV and 10 μA, respectively. An argon ion gun with a voltage of 4 kV, an emission current of 15 mA, and a scan area of 3 X 3 mm^2 was used for depth profiling studies. The sputter rate relative to Ta_2O_5 under the same conditions was approximately 50 Å/ min. Binding energies were corrected for charging effects by referencing to the C_{1s} (284.6 eV) peak, and the determination error of binding energy was ±0.1 eV.

Results and Discussion

Conversion films before and after passivation treatment in PMTA solution were tested with salt water dipping and an H_2S accelerated tarnish test. The results are listed in Table 2 and show that the Mo-S-Cu conversion films possess a certain protective ability against Cl$^-$ or H_2S erosion compared with blank copper. If passivated with PMTA, their protective abilities are greatly promoted and their colors are stabilized.

FT-IR analysis of the conversion films has been discussed in our previous work.[30,31] The stretching vibration frequency of the Mo-S bond for $(NH_4)_2MoS_4$ appears at about 480 cm^{-1}. Because of similarity to the MoO_xS_{4-x} compounds found in the literature,[32] there exists Mo-S-Cu, terminal Mo=S and terminal Mo=O bonds in both the heated and unheated films. The absorption bands emerge at 408–449, 499–562 and 771–
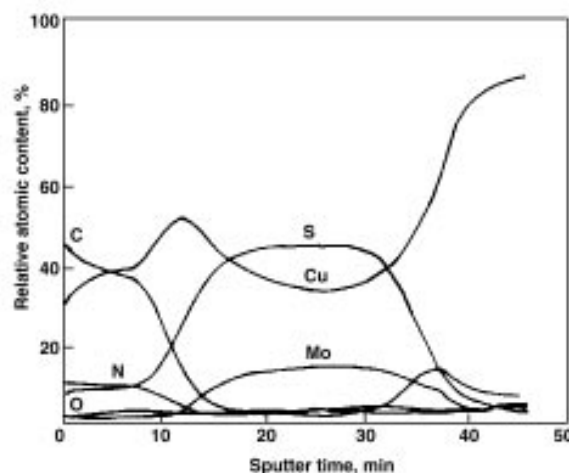

Fig. 4—AES depth profile curves of a PMTA passivated conversion film.

990 cm^{-1}, respectively. The Mo-S-Cu bond indicates that MoS_4^{-2} reacted with a copper surface. The Mo=O bond suggests that some of the sulfur atoms in MoS_4^{-2} units were replaced by oxygen to form $MoO_2S_2^{-2}$, which was linked with the copper surface only by S atoms, while the O atoms were terminal, without any surface bonding action. Therefore, no Mo-O-Cu bridge formed in the films, agreeing with the result of the Mo-S-Cu cluster compounds. To date, no Mo-O-Cu bridge has been found among the known $MoO_xS_{4-x}Cu$ cluster compounds.[25] Therefore, we suggest that these conversion films are cluster compound films because of the formation of Mo-S-Cu bonds. The results of XRD reflection determination show that the films before and after heating treatment are all amorphous.

Figure 1 describes representative Auger electron spectra of the unheated films. Peaks for Mo, S, O, and Cu are still evident after two min of sputtering, while the indication of contaminating carbon disappears. Accordingly, it can be inferred that the cluster compound film is composed of Mo, S, Cu and O. As for a representative heated film (Fig. 2), only Cu, O and contaminating C peaks are strong in its Auger electron spectrum before sputtering, while Mo and S peaks are weak. After 6 min of sputtering, the peak for contaminating C disappears; peaks for molybdenum and sulfur are still weak, while those for Cu and O are strong. This indicates that the film is mainly composed of Cu and O in the profiled depth. After 22.5 min of Ar$^+$ sputtering, however, the peaks for molybdenum and sulfur become strong again, because of penetration of clusters to the inner layer of the film. This indicates that the composition and structure of the conversion films could have been changed by heating treatment.

According to high-resolution XPS and AES determination,[33,34] $Cu_{2p\,3/2}$ and O_{1s} peaks for the blank copper are located at 932.3 and 530.7 eV, respectively. The peak value (336.3 eV) of the CuL_3VV Auger line of Cu_{2p} is identical to that of Cu_2O,[35,36] indicating that the surface of the copper has been oxidized to form a Cu_2O film before being treated in $(NH_4)_2MoS_4$ solution. In fact, it was a Cu_2O layer and not copper atoms with which MoS_4^{-2} reacted. Peak values of $Mo_{3d\,5/2}$, S_{2p}, $Cu_{2p\,3/2}$ and O_{1s} for the unheated films are 231.4,

161.9, 932.5 and 530.5 eV, respectively. Consequently, the valence of each element: Mo, S, Cu and O is +6, -2, +1 and -2, respectively. There also exists a small amount of S^{+4} and S^{+6} on the surface of the films. The films are all multimolecular layers and can be described as an overlapping double-layer structure. The outer (upper) layer has been oxidized to some extent. MoS_4 clusters remain in the inner (lower) layer. The thickness of the films was found to depend on the interface reaction time; longer times resulted in thicker films. As for the heated films, the content, distribution and valence state of each element and the structures of the films changed. The first layer of the heated films is composed almost entirely of CuO. The second layer is a mixture of CuO and Cu_2O. The third is an intermediate. The fourth layer comprises Mo, S, Cu and O; the valence of molybdenum remains ambiguous, while the other three are -2, +1 and -2, respectively. Molybdenum tetrasulfide units survive the heating in this layer. There is still another intermediate layer between the whole film and the copper surface, confirming the penetration of molybdenum and sulfur. Therefore, on the basis of the above analysis, the representative structure schemes of the heated and unheated films are given in Fig. 3. The colors of these films are probably caused by Mo-S-Cu bonds and a statistical distribution and overlapping of various molecular layers, inasmuch as the films are complex multicomponent and multilayer systems. The disparity of colors before and after heating treatment is caused by the change of composition and structure of the films.

Because of the structure of the conversion films, the anticorrosive ability of the colored copper is enhanced, compared to the blank copper; PMTA passivation strengthens this ability. The AES depth profile curves of a PMTA-passivated conversion film are shown in Fig. 4. Two constant composition regions appear around 0.5 to 6.5 and 16.5 to 33.0 min. In the first region, the contents of O and Mo are low and can be neglected; however, the contents of C, N and S are relatively high and can be considered as the characteristic contribution from PMTA molecules. In the second region, the contents of C and N are rather low, while those of S, Cu and Mo are high. This indicates that the depth profile has reached the Mo-S-Cu cluster film. Obviously, a PMTA protective film formed on the colored conversion film.

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Table 2
Results of Accelerated Corrosion & Tarnish Test Of Mo–S–Cu Conversion Films Before & After PMTA Passivation

	Accelerated Test Method	
	Salt water hr^A	H$_2$S tarnish test min^B
Blank copper	3(3) to 5(4)	0.5(4)
Blank copper*	24(0) to 48(1)	180(0–1)
Brown film	5(2)	0.5(4)
Brown film*	80(0) to 108(2)	180(0–1)
Rose film	5(1)	0.5(4)
Rose film*	80(0) to 108(2)	180(0–1)
Blue film	5(1)	0.5(3)
Blue film*	80(0) to 108(1)	180(0–1)
Soft cyan film	5(1)	30(2)
Soft cyan film*	80(0) to 108(1)	180(0–1)
White film	5(1)	30(2)
White film*	80(0) to 108(1)	180(0–1)

* Passivated by PMTA
(A) Parenthetical numbers mean: 0–clear; 1–faintly muddy; 2–lightly muddy; 3–obviously muddy; and 4–very muddy.
(B) Parenthetical numbers mean: 0–no tarnish; 1–faint tarnish; 2–light tarnish; 3–obvious tarnish; and 4–serious tarnish.

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