Investigation on the Various Colored Mo(W)-S Cluster Compound Films on Metal Surface by Spectroscopy

LI Dao-hua

(Xichang College, Xichang 615013, Sichuan)

Abstract: By means of the interface reactions of $Mo(W)S_4^{2-}$ on a metal (copper, steel, zinc, silver, nickel, tin) surface, insoluble cluster compound films were formed with a metallic luster of various colors changing in accordance with the reaction time. 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. Their colors are probably caused by Mo(W)-S-M (M= Cu, Fe, Zn, Ag, Ni, Sn) bonds and a statistical distribution and overlapping of various molecular layers, inasmuch as the films are complex multicomponent and smultilayer systems. Accelerated corrosion tests, LSV, CV, FT-IR, FT-Rmamn; XPS and AES determinations were carried to investigate composition and structure of these conversion films. The results show that bridged Mo(W)-S-M, terminal Mo(W)-S and terminal Mo(W)-O bonds exist in the cluster compound films. The mechanism for films formation and the relationships between these novel films structure and the observed inhibition behavior are discussed.

Key words: Metal surface; Various colors cluster compound films of Mo(W)-S; Spectroscopy

CLC number: O614.81 **Document code**: A

The coloring of metal is currently one of the considerably interesting and important research fields of metal finishing. Conversion films of variety of shades and colors may be applied to metals by thermal treatment, chemical dips and electrolytic process. The films are functional finishing layers, not only providing a decorative or colored finish, but also improving the brightness and cleanness of metal surface, promoting the corrosion resistance and paint or adhesive bonding properties of metals. Classification of coloring treatments can be made on the basis of composition, being either organic or inorganic. Of the many different coloring treatments used, chromate conversion coatings are among the more common Chromates on zinc can vary in color from an almost colorless, blue-white appearance, commonly referred to as single-dip blue, through the yellow iridescent shades, to the heavy olive drab and black types. Dried-in-place, chromate coatings are used on zinc plated steel, hot dip galvanize, unplated steel and aluminum alloys primarily for paint bond improvements. Anodized zinc is an electrolytic process, the coating so formed is very resistant to marine atmospheres and can withstand months of salt spray testing, and also provides protection even at

Received date: 2005-01-09

Foundation item: Major project supported by the Scientific Research Fund (2004A044; 2002A114); Youth Fund (2000-B33) from the Educational Bureau of Sichuan Province.

elevated temperatures in sharp contrast to chromate conversion coatings. Moreover, the coating becomes more electrically resistant as it builds in thickness during the treating process. High dielectric strength is another property of the coating. Molybdates are used to produce attractive black finishes on zinc and cadmium surfaces. The coatings are relatively hard, but thin and not resistant to salt spray testing or outdoor environments without organic topcoats.

1 Experimental

Copper(steel, zinc, silver, nickel, tin) plates (2 ×2 cm; 0.5 mm thick) were polished mechanicaily with fin MgO powder, chemically degreased with acetone and washed in deionized water. Then, the plates were dipped in a 10% H_2SO_4 solution for 20 s and rinsed with deionized water. The washed plates were immediately immersed in a 0.004 mol/L of $(NH_4)_2MoS_4$ or $(NH_4)_2WS_4$ solution at 25℃ for different treatment times. After being withdrawn form the $(NH_4)_2MoS_4$ or $(NH_4)_2WS_4$ solution, the plates were rinsed with water and acetone respectively, and dried immediately by a cold air blast. Cluster compound films of various colors depending on the reaction time were obtained on the copper surface. Then, the films were heated at 100℃ (Mo-S-Cu films) or 150℃ (W-S-Cu films) for different time, the variation sequence of their colours are also given in Table 1.

A Nicolet 170 SX FT-IR spectrometer was used to determine the reflection and transmission spectra (resolving power $4cm^{-1}$). An ESCALAB MK-II electron spectrometer with a Mg 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 10μA, respectively. An argon ion gun with a voltage of 4 kV, an emission current of 15 mA, and a scan area 3×3 mm^2 was used for depth profiling studies. The sputter rate relative to Ta_2O_5 under the same condition was approximately 5nm/min. Binding energies were corrected for charging effects by referencing to the C1s (284.6 eV) peak, and the determination error of binding energy was ±0.1eV.

2 Results and discussion

By means of the interface reactions of $Mo(W)S_4^{2-}$ on a metal (copper, steel, zinc, silver, nickel, tin) surface, insoluble cluster compound films were formed with a metallic luster of various colors changing in accordance with the reaction times. Furthermore, the colors of the films changed gradually with heat treatment. These results are listed in Table 1. The colors of these films are probably caused by Mo(W)-S-Cu (Fe, Zn, Ag, Ni, Sn) 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 cause by the change of composition and structure of the films.

Table 1 Variation sequence of colors cluster compound films

Reaction time/min	Color of unheated film	Colors sequence heated in air
Mo-S-Cu film		
5	Brown	→Rose red→rose purple→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→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
Mo-S-Fe film		
5	Red brown	→Dark red→blue→purple blue
10	Puce	→Light yellow→purple blue
30	Dark green	→Green→light purple→purple red
50	Grey black	→Blue black
W-S-Fe film		
5	Golden yellow	→Brown→blue purple
20	Orange	→Orange red→blue→purple blue
50	Green	→Blue
480	Black	→Black
Mo-S-Zn film		
5	Orange red	→Light purple→light yellow→brown yellow→yellow
10	Golden yellow	→Red brown→purple→purple blue→blue
30	Red brown	→Purple red→light blue→blue
60	Purple	→Purple→light purple→rose red
100	Grey green	→Light green→blue→blue white
W-S-Zn film		
5	Red brown	→Brown→rose red→purple red→blue purple
30	Purple red	→Light yellow→red brown→purple red→blue
60	Blue	→Blue purple→light purple
120	Green	→Light green→blue green→blue white
Mo-S-Ag film		
20	Thick grey	
W-S-Ag film		
120	Grey	
Mo-S-Ni film		
30	Grey black	
W-S-Ni film		
100	Light black	
Mo-S-Sn film		
20	Golden yellow	
W-S-Sn film		
120	Light yellow	

Accelerated corrosion and tarnish tests (Table 2) indicate that the Mo (W)-S films possess a certain protective ability against Cl^- or H_2S erosion. If passivated with PMTA (1 -phenyl -5 -mercaptotetrazole), the protective abilities of these Mo(W)-S-Cu films are greatly promoted and their colors are stabilized. The films are functional finishing layers, which possess decorative, and promote the anticorrosive ability of the metals. Therefore, these films may be applied for finishing and passivation of the metal.

Table 2 Results of accelerated corrosion test of the colour cluster compound films

Specimen	Salt water/hr[A]	H_2S tarnish test/min[A]	$CuSO_4$ point drop test/s
Blank copper	3(3) to 5(4)	0.5(4)	
Mo-S-Cu film			
Brown	5(2)	0.5(4)	
Brown*	80(0)-108(2)	180(0-1)	
Rose	5(1)	0.5(4)	
Rose*	80(0)-108(2)	180(0-1)	
Blue	5(1)	0.5(3)	
Blue*	80(0)-108(1)	180(0-1)	
Soft cyan	5(1)	30(2)	
Soft cyan*	80(0)-108(1)	180(0-1)	
White	5(1)	30(2)	
White*	80(0) -108(1)	180(0-1)	
W-S-Cu film			
Orange	3(0)-5(2)-7(3)-12(4)	1(4)	
Orange*	72(0)	180(0)	
Orange red	3(0)-5(1)-7(2)-12(4)	1(4)	
Orange red*	72(0)	180(0)	
Rose	3(0)-5(1)-7(2)-12(4)	1(1)-30(2)	
Rose*	72(0)	180(0)	
Silver white	3(0)-5(1)-7(2)-12(4)	10(1)-30(2)	
Silver white*	72(0)	180(0)	
Golden yellow	3(0)-5(1)-7(2)-12(4)	10(1)-30(2)	
Golden yellow*	72(0)-108(1)	180(1)	
Blank steel	1(2)-5(4)	1(4)	
W-S-Fe film			
Golden yellow	19(1)-58(3)	15(1)-41(2)	
Orange	16(1)-56(3)	12(1)-34(2)	
Green	13(1)-47(3)	10(1)-27(2)	
Black	16(1)-57(3)	12(1)-36(2)	
Blank zinc	0.5(2)-3(4)	1(4)	<1
Mo-S-Zn film			
Orange red	13(1)-5(2)-36(4)	12(1)-20(2)-33(4)	52
Golden yellow	18(0)-41(1)-78(3)	16(0)-32(2)-56(3)	96
Red brown	16(1)-30(2)-53(4)	15(1)-25(2)-33(4)	70
Purple	15(1)-28(2)-49(4)	12(1)-23(2)-35(4)	68
Grey green	13(0)-26(2)-43(4)	13(1)-26(2)-37(4)	57
W-S-Zn film			
Red brown	17(1)-28(2)-43(4)	15(1)-26(2)-38(4)	65
Purple red	21(1)-30(2)-41(4)	15(1)-28(2)-40(4)	70
Blue	19(1)-31(2)-40(4)	18(1)-31(2)-41(4)	69
Green	22(1)-32(2)-41(4)	19(1)-30(2)-45(4)	79

* *Passivated by PMTA*

(A) ***Parenthetical numbers mean: 0-no tarnish; 1-faint tarnish; 2-light tarnish; 3-obvious tarnish; 4-serious tarnish.***

Insoluble conversion films of Mo(W)-S cluster compounds with a metallic luster of various colors have been obtained from the interface reactions between Mo (W)S_4^{2-} inos and metal surface. These films are functional finishing layers, not only possessing decorative properties, but promoting the anticorrosive ability of the metals as well. Therefore, they be applied for finishing and passivation of steel surface. By means of the analogous method, black Mo (W)-S-Ni cluster compound films have been applied to the surface of nickel.

FT-IR, F-IR, FT-Raman, XPS and AES determinations were carried out to investigate these conversion films before and after heating treatment. The results show that bridged Mo(W)-S, terminal Mo(W)-S and terminal Mo(W)-O bonds exist in the cluster compound films. The thickness, composition and valence state of each element of various Mo(W)-S cluster compound films are listed in Table 3. The colors of the films varied with their compositions and thicknesses, and the thickness was found to depend on the reaction time: the longer the time, the thicker the films. Hence, it is reasonable that the surface films are multimolecular layers formed by coordination reactions of Mo $(W)S_4^{2-}$ on the metal surface. The outer molecular layers have been oxidized to some extent, while MoS_4 and WS_2 units are maintained in the inner layers. Their colors are probably caused by Mo (W)-S-M bonds and a statistical distribution and overlapping of various molecular layers since the films are complicated multicomponent and multilayer systems.

Table 3 The thickness, composition and valence state of each element of various films

Specimen	Film thickness (nm)	Composition (A.C.%)				Valence state of the elements							
						outer				inner			
Mo-S-Cu film		*Cu*	*Mo*	*S*	*O*	*Cu*	*Mo*	*S*	*O*	*Cu*	*Mo*	*S*	*O*
Brown	86	42.1	12.1	31.9	13.7	+1,+2	+6	+6,+4,-2	-2	+1	+6	-2	-2
Rose	109	38.2	13.0	30.8	17.8	+1,+2	+6	+6,+4,-2	-2	+1	+6	-2	-2
Soft cyan	178	45.1	9.2	33.9	11.6	+1,+2	+6	+6,+4,-2	-2	+1	+6	-2	-2
White	236	40.2	11.2	36.2	12.2	+1,+2	+6	+6,+4,-2	-2	+1	+6	-2	-2
W-S-Cu film		*Cu*	*W*	*S*	*O*	*Cu*	*W*	*S*	*O*	*Cu*	*W*	*S*	*O*
Orange	56	31.8	17.8	43.4	6.8	+1,+2	+6	+6,+4,-2	-2	+1	+6	-2	-2
Rose	78	30.6	19.1	40.2	9.9	+1,+2	+6	+6,+4,-2	-2	+1	+6	-2	-2
Golden yellow	92	29.5	19.6	42.6	8.1	+1,+2	+6	+6,+4,-2	-2	+1	+6	-2	-2
Mo-S-Fe film		*Fe*	*Mo*	*S*	*O*	*Fe*	*Mo*	*S*	*O*	*Fe*	*Mo*	*S*	*O*
Red-brown	175	26.3	14.3	33.6	25.6	+3	+6	+4,+6,-2	-2	+2	+4,+6	-2	-2
Grey-black	330	39.8	12.3	32.5	15.7	+3	+6	+4,+6,-2	-2	+2	+4,+6	-2	-2
Blue*	225	49.2	9.9	3.4	37.3	+3	+6	+4,+6,-2	-2	+2	+4,+6	+6,-2	-2
W-S-Fe film		*Fe*	*W*	*S*	*O*	*Fe*	*W*	*S*	*O*	*Fe*	*W*	*S*	*O*
Golden-yellow	225	30.3	19.8	23.1	26.7	+3	+6	+4,+6,-2	-2	+2	+4,+6	-2	-2
Orange	245	20.8	17.0	28.9	33.2	+3	+6	+4,+6,-2	-2	+2	+4,+6	-2	-2
Black	500	18.3	25.2	31.2	25.1	+3	+6	+4,+6,-2	-2	+2	+4,+6	-2	-2
Blue-purple**	300	45.1	15.9	3.8	35.1	+3	+6	+4,+6,-2	-2	+2	+4,+6	+6-2	-2
Mo-S-Zn film		*Zn*	*Mo*	*S*	*O*	*Zn*	*Mo*	*S*	*O*	*Zn*	*Mo*	*S*	*O*
Golden yellow	60	32.5	19.3	39.4	8.5	+2	+6	+4,+6,-2	-2	+2	+4,+6	-2	-2
Red brown	107	22.5	23.3	36.3	17.5	+2	+6	+4,+6,-2	-2	+2	+4,+6	-2	-2
Purple	261	27.1	21.3	38.1	13.3	+2	+6	+4,+6,-2	-2	+2	+4,+6	-2	-2
W-S-Zn film		*Zn*	*W*	*S*	*O*	*Zn*	*W*	*S*	*O*	*Zn*	*W*	*S*	*O*
Red brown	75	31.6	21.0	39.1	8.1	+2	+6	+4,+6,-2	-2	+2	+4,+6	-2	-2
Purple red	182	23.5	29.2	32.6	14.5	+2	+6	+4,+6,-2	-2	+2	+4,+6	-2	-2
Green	392	29.2	23.0	36.1	11.5	+2	+6	+4,+6,-2	-2	+2	+4,+6	-2	-2
Mo-S-Ni film		*Ni*	*Mo*	*S*	*O*	*Ni*	*Mo*	*S*	*O*	*Ni*	*Mo*	*S*	*O*
Grey black	185	25.6	22.0	40.9	11.3	+2	+4,+6	-2	-2	+2	+4,+6	-2	-2

* **arising from the Red-brown film heated by air at 250℃ for 2hr;**

* * **arising from the Golden-yellow film heated by air at 250℃ for 2hr.**

With regard to the heated films, there also exist Mo(W)-S- Cu (Fe, Zn, Ag, Ni, Sn) bonds. The composition and valence state of the elements were unchanged, while the structure and the distribution of each element were changed. Furthermore, there is another intermediate layer between the whole film and the metal surface, confirming the penetration of Mo(W) and S to the depth of substrate, which increases the thickness of the films.

3 Conclusion

Cluster compound film of various colors have formed by the interface reaction of MoS_4^{2-} and WS_4^{2-} with the Cu_2O layer on the surface of copper. The nature of the reaction is the formation of Mo(W)-S- Cu (Fe, Zn, Ag, Ni, Sn) coordination bonds. The cluster compound films are composed of Mo (W), S, Cu (Fe, Zn, Ag, Ni, Sn) and O, showing +6, −2, +1(+2, +2, +1, +2, +2) and −2 valency, respectively. The films are all complicated multimolecular layers and can be described as two overlapping layers.

References

〔1〕J. W. Mcdonald, G. D. Friese, L. D. Rosenhein and W. E. Newton, inorg. Chim. Acta, 1983,72:205.

〔2〕A. Muller, E. Diemann, R. Jostes and H. Bogge, Angew. Chem. int. Ed. Engl., 1981,20:934.

〔3〕Kouigen, E., et al., Angew. Chem., lnt. Ed. Engl., 1976,15:680.

〔4〕〔11〕A. Muller and S.Saukat, Angew. Chem. lnt. Ed. Engl.,1977,16:705.

〔5〕Urgen M, Stole U, Kirchheim R.Corros. Sci., 1990,30:377.

〔6〕C. D Wagner, W. M. Riggs, L. E. Daris, J. F. Moulder and G. E. Muilenberg. Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer Corp., Eden Praries,MN,1979.

〔7〕Brumdli, C. R., Surf. Sci., 1977,68:459.

〔8〕Genebour A, Fauchcu J, Ben Bachir A. Corrosion, 1998, 44(4):214.

金属表面Mo(W)-S彩色簇合物膜的光谱研究

李道华

(西昌学院，四川 西昌 615013)

【摘 要】$Mo(W)S_4^{2-}$与金属M (M= Cu、Fe、Zn、Ag、Ni、Sn)表面发生配位化学反应，得到不溶性且具有装饰效果的Mo(W)-S彩色簇合物膜。随着反应时间或加热时间的变化，膜呈现不同的具有金属光泽的颜色。这种膜层属于功能性修饰层，不仅赋予金属表面以美观的外表，而且提高表面的光洁度和清洁度，增强金属的抗腐蚀性能。本文采用加速腐蚀实验、LSV、CV、FT-IR、FT-Raman、XPS和AES研究了$Mo(W)S_4^{2-}$在金属表面的成键特征和波谱变化，探讨了簇合物膜的组成、性能、结构、化学状态和形成机理。结果表明，膜层中存在桥基Mo(W)-S-M键、端基Mo(W)-S和Mo(W)-O键。膜为多分子层组成的复杂体系，其颜色是各组分统计分布的结果。

【关键词】金属表面；彩色簇合物膜；光谱

【中图分类号】O614.81 【文献标识码】A 【文章编号】1673-1891(2005)01-0095-06

收稿日期：2005-01-09

基金项目：四川省教育厅自然科学重点科研基金(2004A044,2002A114)和四川省教育厅青年基金(2000-B33)资助项目。

作者简介：李道华(1966-)，男，教授。研究方向：金属表面配位化学、纳米材料、分子结构和高等教育教学研究。