A Protective-Decorative Chemical Conversion Film Of Si-Mo Heteropoly Acid on Steel

By J.L. Fang, J.K. Wang, T.Q. Liu and Y. Wu

A decorative chemical conversion film was formed on A3 mild steel by immersing it in a Si-Mo heteropoly acid solution. The SEM photographs and anodic polarization curves revealed the good anticorrosive property of the film. The results of XPS and AES analyses showed that Fe existed as Fe(II) and Fe(III) in the film, while Mo as Mo(VI) was present in the surface of the film, with Mo(VI) and Mo(IV) in the internal layer of the film. The relative atomic percent content of the film obtained from the elemental composition constant region of the profile curves by AES was 17 percent iron, 13 percent molybdenum, 9 percent silicon, and 60 percent oxygen.

To protect metals from corrosion, chromate was used extensively as a chemical surface treating agent or passive agent, because it can form excellent protective chemical conversion films on various metal surfaces. The main disadvantage of the chromate system is the serious toxicity of the processing solution. In the last few years, the molybdate, tungstate, vanadate, etc., oxy-acid anions[1,2] and organic compounds[3-6] have been found to be effective surface protective agents for various metals. Wilcox and Gabe[7] have published a review of corrosion inhibition of the molybdate conversion film. The protective mechanism of molybdate is attributed to the molybdenum oxide film formed on an iron surface. The valence state of molybdenum in surface films varies for different metal surfaces.

Heteropoly acid is a polynuclear coordination compound with an oxygen bridge. It possesses excellent oxidation-reduction,[8] film-forming,[9] catalytic,[10] ion exchange,[11] and antivirus and antitumor[12] characteristics. Kurosawa *et al.* obtained a more adhesive and protective chemical conversion film from 0.1 mol/L Na_2MoO_4 + H_3PO_4 solution than from molybdate solution alone.[13] The results of AES and IR showed that the film is composed of MoO_4^{-2}, PO_4^{-3}, $FeO \cdot OH$ and MoO_3. Some authors have indicated that the effect of heteropoly molybdate was better than molybdate alone.[14,15] Xu reported that the protective ability of P-Mo heteropoly acid on steel is better than that of molybdate and phosphate alone, and that the protective film is composed of $Fe_n[PMo_xO_y]$ or $M_n[PFeMo_xO_y]$, where $M = K^+, Na^+$.[16] Lizloves indicated that $Na_3PMo_{12}O_{40}$ can decrease the corrosion of stainless steel in H_2SO_4.[17]

This paper reports investigation of the corrosion resistance, composition and elemental valence states of the conversion film of Si-Mo heteropoly acid on A3 mild steel.

Experimental Procedure

Preparation of Reagents and Specimens

$H_3[PX_{12}O_{40}] \cdot nH_2O$, where X = W, Mo, is an analytical reagent, and $H_8SiW_{12}O_{42} \cdot nH_2O$, $H_8SiMo_{12}O_{40} \cdot nH_2O$, $K_{15}[Ce(HSiW_9O_{34})_2] \cdot 28H_2O$ and $Na_{3+n}PMo_{12-n}V_nO_{40}(n = 0\sim5)$ were prepared according to Ref. 18. After the A3 mild steel specimens*, 2 x 5 x 0.2 cm, were polished mechanically with fine grit paper, they were chemically degreased for 10 min at 80 °C and washed in deionized water. The washed specimens were then dipped in 5-percent HCl and rinsed with deionized water. The specimens were immediately dipped in 2 g/L of heteropoly acid solution at room temperature for a 5-min passivation treatment. Finally, the specimens were dried by air blast. Following these preparations, different tests were performed.

Accelerated Corrosion Test[4]

An accelerated H_2S corrosion test was carried out in a glass vacuum desiccator for 40 hr, in which the concentration of H_2S was one percent.

$CuSO_4$ Spot Test

One drop of test solution (10% $CuSO_4 \cdot 5H_2O$, 40 mL/L; 10% NaCl, 20 mL/L; 0.1 mol/L HCl, 1 mL/L) was placed into five test regions (~0.5 cm^2) each insulated with wax on the specimen surface, and the elapsed time to red copper coating was recorded; the longer the time, the more anti-corrosive the passive film.

Electrochemical Measurement

Anodic corrosion of the treated and untreated A3 steel specimens with heteropoly acid solution was determined with a potentiostat/galvanostat. The steel was used as the research electrode, a platinum panel as the auxiliary electrode and a saturated calomel electrode as the reference. The electrolytic solution was

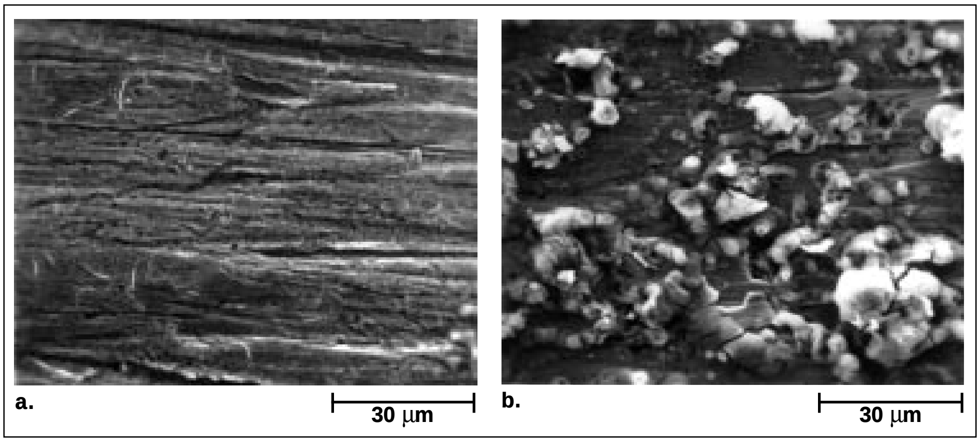

Fig. 1—SEM photographs of specimens after H_2S gas corrosion: (a) with film coating; (b) blank.

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* (C 0.16%; Mn 0.47%; Si 0.23%; P 0.017%; S 0.015%)

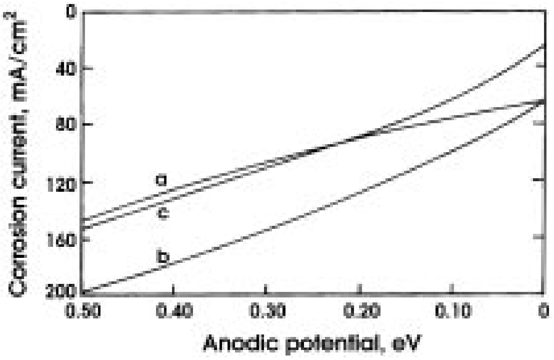

Fig. 2—Corrosion current variation with anode potential: (a) filmed iron electrode; (b) blank; (c) chromate.

Results of Accelerated Corrosion Tests Of Heteropoly Acid Films

Acid	$CuSO_4$ Spot Test(s)	Acid	$CuSO_4$ Spot Test(s)
Blank	<1	$Na_3PMo_{12}O_{40}$	1.5
$H_3[PW_{12}O_{42}] \cdot nH_2O$	1	$Na_4PMo_{11}VO_{40}$	5
$H_3[PMo_{12}O_{42}] \cdot nH_2O$	5	$Na_5PMo_{10}V_2O_{40}$	11
$H_8SiW_{12}O_{42} \cdot nH_2O]$	1.5	$Na_6PMo_9V_3O_{40}$	3
$H_8[SiMo_{12}O_{40}] \cdot nH_2O$	15	$Na_7PMo_8V_4O_{40}$	3.5
$K_{15}[Ce(HSiW_9O_{34})_2] \cdot 28H_2O$	1	$Na_8PMo_7V_5O_{40}$	1

3-percent NaCl. The scanning voltage was 0–0.5 V, scanning speed was 50 mV/sec.

Electron Spectroscopy Analysis[6]

An electron spectrometer with an aluminum X-ray anode (energy of Al Kα, 1486.6 eV) was used for measurements. Survey and high-resolution spectra were obtained with the energy analyzer operating in a constant transmission energy mode at pass energies of 100 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 were 10 kV and 40 mA, respectively. An argon ion gun with a voltage of 4 kV, an emission current of 15 mA, and area 5 x 5 mm was used for depth profile studies. The sputter rate, relative to Ta_2O_5 under the same conditions, was approximately 0.005 µm/min (50 Å/min). Binding energies were corrected for charging effects by reference to the C_1 $_{sec}$(284.8 eV) peak. The determination error of binding energy was ±0.1 eV.

Results and Discussion

Comparison of Anticorrosion Abilities

Specimens passivated in 2 g/L, at pH 1.5, of various, heteropoly acid solutions at 10 °C for 5 min, were tested with the $CuSO_4$ Spot Test. The results are listed in the table. As can be seen, film formed in $H_8[SiMo_{12}O_{40}]$ solution was more effective than other heteropoly acids. The film formed was a good decorative blue-violet.

Film Morphology

The topography of a corroded blank specimen and chemical conversion film from 1.2 g/L of $H_8[SiMo_{12}O_{40}] \cdot nH_2O$ solution at 38 °C, pH 5, for 4 min was examined by scanning electron microscope (SEM). It can be seen (Fig. 1) that the blank specimen surface was seriously corroded, with the diameter of corroded particles was about 15 µm. The surface of the heteropoly acid film is almost uncorroded by H_2S, demonstrating that the film of Si-Mo heteropoly acid possesses excellent anticorrosive properties.

Electrochemical Corrosion of Si-Mo Heteropoly Acid Film

The curves of anodic corrosion current variation of blank and filmed specimens with anodic potential were determined by a linear scanning method. The results are shown in Fig. 2, where it can be seen that the corrosion current of the filmed iron electrode is obviously smaller than that of the blank iron electrode at the same anodic potential. The Si-Mo heteropoly acid film is, consequently, an anticorrosive film.

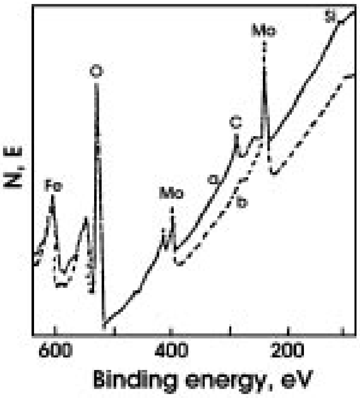

Fig. 3—Survey XPS spectra of heteropoly acid passive film: (a) before sputtering; (b) after 10 min sputtering.

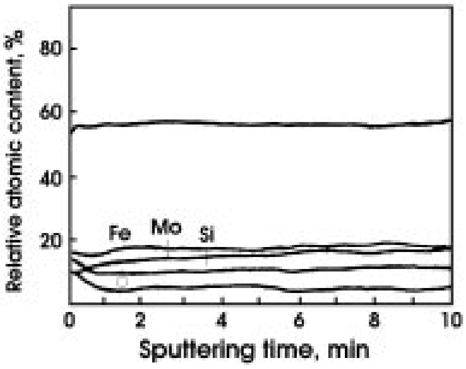

Fig. 4—AES composition depth profile of passive film.

Analysis of Si-Mo Heteropoly Acid Film

1. Composition of the Passive Film

The elemental composition of the Si-Mo heteropoly acid passive film formed on the A3 steel surface before and after argon ion sputtering was determined with XPS; the results are shown in Fig. 3. Quantitative determinations by AES of the elements in the surface film are shown in Fig. 4 as a function of sputtering time. Figure 3 shows that there are Fe, O, Mo, Si and C in the film before sputtering, but that the C peak almost disappears after sputtering. From Fig. 4, it can be seen that the carbon content decreased rapidly after one min of Ar^+ sputtering, and is close to the base line of the AES depth profile curve. This indicates that the contamination by carbon existed on the surface layer, and that the trace amount of carbon comes from the A3 mild steel, possibly after sputtering one min. The content (relative atomic content) of O, Fe, Mo, Si and C was nearly constant after one min of Ar^+ sputtering, which indicates that the passive film is homogeneous. Therefore, the real composition of the passive film can be established from the constant composition region between 2 to 10 min in the sputtering profile curves (percent): O, 60; Fe, 17; Mo, 13; Si, 9 and C, 3. The atomic number ratio obtained from these results is Si:Mo = 2.2:1, which disagrees with the ratio (1:12) of the $H_8[SiMo_{12}O_{40}] \cdot nH_2O$ heteropoly acid molecule, indicating that the surface passive film is not composed simply of the ferrous salt of Si-Mo heteropoly acid.

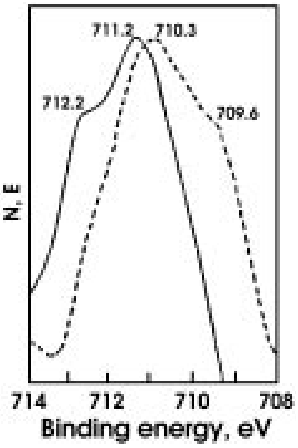

Fig. 5—High-resolution XPS spectra of Fe in passive film: (a) before sputtering; (b) after 10 min sputtering.

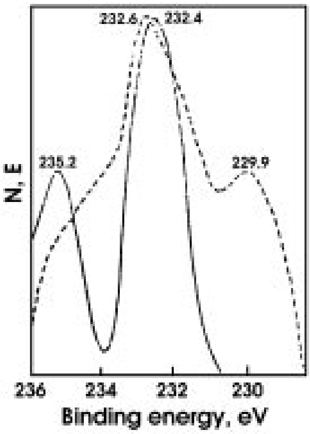

Fig. 6—High-resolution XPS spectra of Mo in passive film: (a) before sputtering; (b) after 10 min sputtering.

2. Valence States in Passive Film

To determine the valence state of iron and molybdenum in the film, high resolution XPS spectra of the two elements were determined (Figs. 5 and 6). From Fig. 5, it can be seen that there are two valence states of iron before Ar$^+$ sputtering. The binding energy of the main peak is above 711.2 eV and is identical with the binding energy of 710.8 to 711.2 eV[19] of Fe(III) in Fe_2O_3. A side peak at 712.2 eV is close to the measured binding energy (712.0 eV) of Fe(II) in $FeSO_4$. After Ar$^+$ sputtering, the Fe(II) peak (712.2 eV) disappeared. The Fe(III) peak (710.8 eV) is still the main peak, but a new Fe(II) peak has occurred at 709.6 eV.[20] Therefore, two valence states of iron existed internally and on the surface of the film and the amount of Fe(III) is greater than that of Fe(II).

In Fig. 6, there are two molybdenum peaks of 232.4 and 235.2 eV before Ar$^+$ sputtering. They are identical with that of 3d 5/2 (232.2 to 232.7 eV) and 3d 3/2 (235.6 eV) of MoO_4^{-2},[19] which demonstrates that Mo(VI) existed in the surface layer of the passive film. After sputtering, the Mo(VI) peak of 232.6 eV is still the main peak, but the peak of 235.2 eV has disappeared and a new peak of 229.9 eV has appeared, close to MoO_2 (229.95 eV).[19] These values show that there are Mo(VI) and Mo(IV) in the internal layer of the passive film. This may be attributed either to reduction of the Si-Mo heteropoly acid by iron or to reduction of molybdenum by Ar$^+$ sputtering.

Findings

A Si-Mo heteropoly acid ($H_8[SiMo_{12}O_{40}] \cdot nH_2O$) was more effective for preventing corrosion of A3 mild steel than other P-W, P-Mo, Si-W, Ce-Si-W, P-Mo-V heteropoly acids. A 5-min treatment in 2 g/L of $H_8[SiMo_{12}O_{40}] \cdot nH_2O$ solution at room temperature formed a decorative blue-violet chemical conversion film on the steel. The SEM photographs and anodic polarization curves revealed the good anticorrosive property of the film. The results of XPS and AES analyses showed that Fe existed as Fe(II) and Fe(III) in the film, while Mo as Mo(VI) was in the surface of the passive film, but as both Mo(VI) and Mo(IV) in the internal layer of the film. The relative atomic percent from the constant region of the profile curves by AES was Fe, 17; Mo, 13; Si, 9; and O, 60, respectively.

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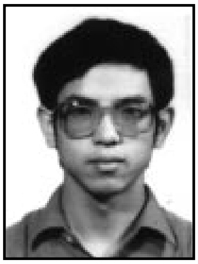
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