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A Study of the Chemical Composition of the Passive Film on a Ti-Mo Alloy in HCl and H_2SO_4

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The composition of the passive film on Ti-15Mo alloy, formed in 1 mol/L and 4mol/L HCl and 2 mol/L H_2SO_4 solutions at 70 °C (160 °F) under anodic polarization is investigated by XPS and electrochemical techniques. Anodic polarization potential is found to have an obvious influence on the content of Mo in the film. At lower anodic polarization potentials, the surface of the passive film is enriched in Mo. However, at higher anodic polarization potentials, the surface is diluted in Mo. The anions of the electrolytes influence the composition of the passive film. In HCl solution, chloride ions are incorporated with the passive film during its formation. The passive film consists of a compound containing chloride and oxide ions. While in H_2SO_4 solution, the passive film only consists of titanium-molybdenum oxide. Sulfide ions and other sulfur are not incorporated. Ti-Mo alloys have a better passivity than pure Ti in HCl and H_2SO_4 solutions. This passivity is related to the enrichment of Mo in the surface of the passive film.

Keywords
passive film, Ti-Mo alloy, XPS

1. Introduction

THE ADDITION of Mo (15 to 32 wt%) to pure titanium enhances the corrosion resistance in reducing acids. For example, the corrosion rate of Ti-Mo alloy containing 20 wt% Mo is 10 to 100 times lower than that of pure titanium in hot-concentrated hydrochloric acid, medium-concentrated sulfuric acid and acidic brine of Salt Lake (Ref 1, 2). The excellent corrosion resistance of Ti-Mo alloy in reducing acids is attributed to its passivity. Therefore, an investigation of the passive film of Ti-Mo alloy has a certain theoretical and practical significance. Previously, a large number of the studies on passive films have been carried out for iron, Fe-Cr stainless steel or titanium (Ref 3-6). Hashimoto et al. (Ref 7, 8) investigated the corrosion behavior and the passive film on Ti-Ni and Ti-Cr alloys. A little work on passive film of Ti-Mo alloy was also reported. At present, the influence of Mo on the formative process, the composition and structure and the electric properties of the passive film formed on Ti-Mo alloy is not well understood. The present work uses x-ray photoelectron spectroscopy (XPS) and electrochemical techniques to study the passive film on Ti-Mo alloys containing 15 wt% Mo in HCl and H_2SO_4.

2. Experiments

2.1 *Materials and Solutions*

Solution heat treated Ti-15Mo alloy is used for the test specimens. The nominal composition in wt% is as follows: 16.49Mo, 0.02C, 0.12Fe, 0.01Si, and remainder Ti. The test solutions of 1 and 4 mol/L HCl and 2 mol/L H_2SO_4 are prepared from reagent grade 36 to 38% HCl, 98% H_2SO_4, and water, respectively. All tests are performed at 70 ± 1 °C (160 ± 2 °F).

2.2 *Electrochemical Measurement*

The Princeton Electrochemical Measurement System with software M352 (Princeton Applied Research Corp., Princeton, NJ) is used to perform the measurements of the polarization curves. A saturated calomel electrode (SCE) and saturated mercurous sulfate electrodes (Hg/Hg_2SO_4) are used as reference electrodes in HCl and H_2SO_4, respectively. The sample is cathodically polarized at 5 mA/cm^2 for 5 min to dissolve the air-formed oxide. After that, the sample is held at open circuit potential for 5 min to desorb the monolayer of hydrogen that deposits on the surface during cathodic reduction. Scanning speed is 0.5 mV/s. Another potentiostat (model HDV7C; San Ming Second Radio Factory, San Ming City, Fujian Province, P.R. China) is used to perform anodic polarization at a constant potential.

2.3 *XPS Surface Analysis*

Soon after 24 h testing of anodic polarization at the constant potential, the sample is removed from the test cell before disconnecting the circuit, rinsed in doubly distilled water, and dried with argon blowing. The sample is then stored in a desiccator for a maximum time of 2 h before being introduced into the surface analysis apparatus and immediately analyzed. XPS analysis is performed in a PHI 5000 ESCA system (Perkin Elmer Corp., Norwalk, CT) with MgKα excitation. The spectrum scanning of XPS and depth profiles with Ar^+ ions sputter is performed in turns. Sputter rate is 1 or 0.2 nm/min. By ion bombardment on the sample, the depth profiles are obtained, and the change of composition with the film thickness and the enrichment or depletion of alloy constituents in passive film are revealed. PE-7000 software (Perkin Elmer Corp., Norwalk, CT) is used for spectrum analysis.

3. Experimental Results and Discussion

3.1 *Electrochemical Measurement*

The potentiodynamic polarization curves of Ti-15Mo alloy at 70 °C (160 °F) in 1 and 4 mol/L HCl and 2 mol/L H_2SO_4 are presented in Fig. 1, in which the curves of Ti and Mo measured on the same conditions are also shown. As can

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Table 1 Atomic percent and weight percent of Ti 2p, Mo 3d, Cl 2p, and O 1s as measured by the spectrum scanning of XPS and depth profiling with Ar^+ ion sputtering performed by turns

Medium	Potential,	Sputtering	Ti 2p		Mo 3d		Cl 2p		O 1s		
70 °C (160 °F)	V	depth, nm	at. %	wt %	at. %	wt %	at. %	wt %	at. %	wt %	f(Mo)
4 mol/L HCl	0.000	0	20.98	38.90	3.04	11.29	3.68	5.05	72.29	44.77	1.34
		1	23.36	42.09	3.05	11.01	3.54	4.72	70.05	42.18	1.26
		2	23.92	42.76	3.07	11.00	3.61	4.76	63.39	41.46	1.24
		4	24.99	44.17	3.10	10.96	3.31	4.33	66.60	40.52	1.22
	+0.900	0	7.16	30.31	0.47	3.99	4.89	15.33	35.60	50.37	0.70
		2	16.66	44.62	1.45	7.78	3.91	7.75	44.51	39.84	0.90
		4	17.96	47.18	1.98	10.41	2.90	5.63	41.93	36.77	1.10
		6	19.93	51.20	2.47	12.71	2.42	4.60	38.68	31.49	1.22
1 mol/L HCl	–0.100	0	13.03	25.44	4.96	19.40	2.06	3.01	79.93	52.15	2.63
		1	16.91	31.97	4.47	16.93	1.86	2.60	76.76	48.50	2.11
		2	16.12	30.70	4.55	17.37	1.85	2.61	77.48	49.32	2.20
		4	16.26	30.71	4.80	18.17	1.65	2.31	77.30	48.81	2.27
	+0.900	0	24.01	45.91	1.30	4.96	1.79	2.53	72.89	46.58	0.59

Note: Sputtering depth is calculated by multiplying sputtering rate and sputtering time. The number of significant figures is one.

Table 2 Atomic percent and weight percent of Ti 2p, Mo 3d, S 2p, and O 1s as measured by the spectrum scanning of XPS and depth profiling with Ar^+ ion sputtering performed by turns

Medium	Potential,	Sputtering	Ti 2p		Mo 3d		S 2p		O 1s		
70 °C (160 °F)	V	depth, nm	at. %	wt %	at. %	wt %	at. %	wt %	at. %	wt %	f(Mo)
2 mol/L H_2SO_4	–0.600	0	18.13	35.60	2.97	11.68	1.42	1.87	77.49	50.85	1.65
		1	17.71	34.70	3.34	13.11	0.76	1.00	78.20	51.19	1.83
		2	17.19	33.54	3.67	14.35	0.78	1.02	78.36	51.09	2.00
		4	17.05	33.08	3.94	15.32	0.57	0.74	78.43	50.86	2.11
	+0.700	0	16.28	35.13	1.49	5.85	0.80	1.14	81.44	57.88	0.94

Note: Sputtering depth is calculated by multiplying sputtering rate and sputtering time. The number of significant figures is one.

be seen, Ti-15Mo alloy possesses a better property of self passivation in HCl and H_2SO_4 solutions at 70 °C (160 °F). The corrosion potentials (Ec) of Ti-15Mo alloy are 100 mV more noble, and the passivating peak currents of Ti-15Mo alloy are over 10 times less as compared with Ti in HCl and H_2SO_4. The passivity of Ti-15 Mo is improved because of alloying with Mo.

3.2 *Results from XPS*

The six alloy (Ti-15Mo) specimens subjected to the following passivating conditions are analyzed by XPS: 1 mol/L HCl at anodic polarization potentials –0.100 and +0.900 V (SCE); 4 mol/L HCl at anodic polarization potentials 0.000 and +0.900 V (SCE); 2 mol/L H_2SO_4 at anodic polarization potentials –0.600 and +0.700 V (Hg/Hg_2SO_4).

The spectra of the six specimens before Ar^+ ions sputtering are shown in Fig. 2. The intense O 1s, C 1s, Ti 2p, Mo 3d, Si 2p, and Si 2s peaks are observed in the spectra. In addition, Cl (Cl 2p) and S (S 2p) peaks are also observed. The atomic percent of Ti 2p, Mo 3d, O 1s, C 12p, and S 2p peaks for HCl and H_2SO_4 are determined by PE-7000 software and are presented in Tables 1 and 2, respectively. Weight percent converted from atomic percent is also shown in the same table.

Tables 1 and 2 show that, for the six passive conditions, the Mo contents (wt%) in the film are different. To characterize the changes of Mo composition in the film, the enrichment factor f(Mo) is defined as (Ref 9):

$$f(\mathrm{Mo}) = \frac{\mathrm{Mo/(Mo + Ti)\ in\ film}}{\mathrm{Mo/(Mo + Ti)\ in\ alloy}} \qquad \text{(Eq 1)}$$

The values of f(Mo), which are calculated from the weight percent of Ti 2p and Mo 3d in Table 1 using Eq 1, are also summarized in the same tables. The anodic polarization potential in a given concentration solution has a great influence on the values of f(Mo). Before Ar^+ ion sputtering, at lower anodic polarization potentials, the values of f(Mo) in the outer layer of the surface of the passive film are all greater than 1. This means that the outer layer of the passive film is enriched in Mo. At higher anodic polarization potentials, the values of f(Mo) are all less than 1, meaning that the surface of the passive film is diluted in Mo. The polarization curves of Mo, Ti, and Ti-15Mo in Fig. 1 show that Mo has a transpassive potential φ_{tp}. When Ti-15Mo alloy is at potentials higher than φ_{tp}, Mo undergoes the transpassive dissolution that results in the depletion in Mo on the surface of the film. At lower anodic polarization potentials, Mo is in the passive region, where the preferential dissolution of Mo does not take place, and the enrichment in Mo appears on the surface of the film.

Table 1 shows chlorine is contained in the passive films of the specimens in HCl solution. The maximum content and

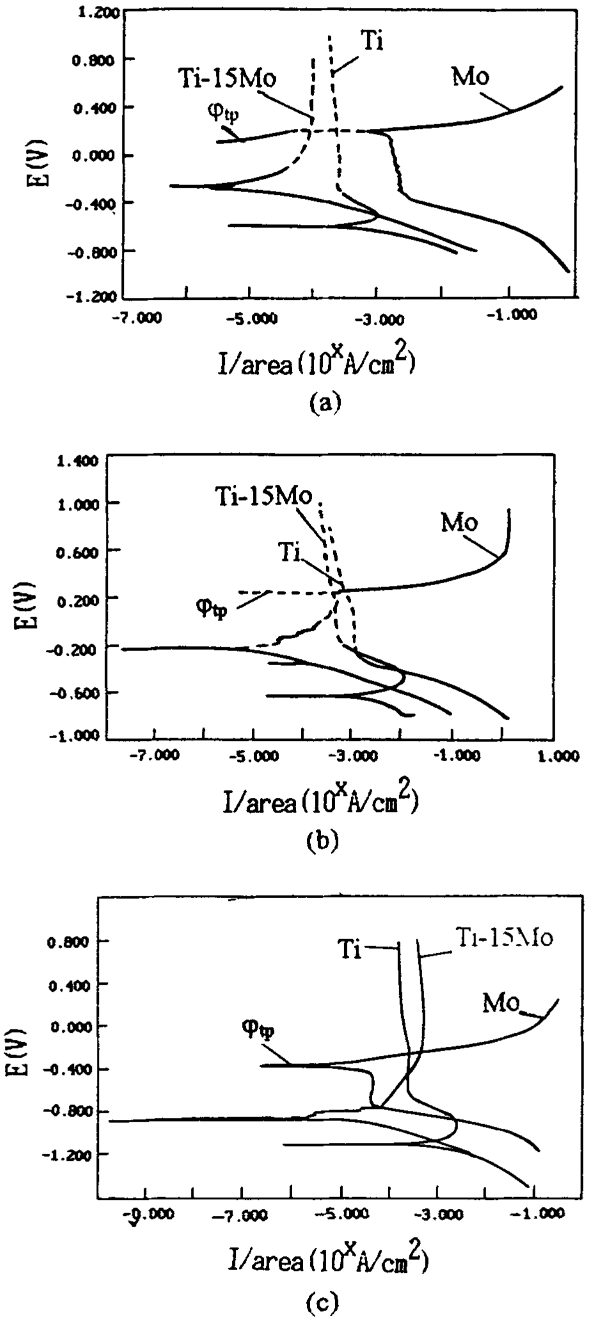

Fig. 1 Polarization curves of Ti-15Mo alloy, Ti, and Mo at 70 °C (160 °F): (a) 1 mol/L HCl, (b) 4 mol/L HCl, (c) 2 mol/L H_2SO_4

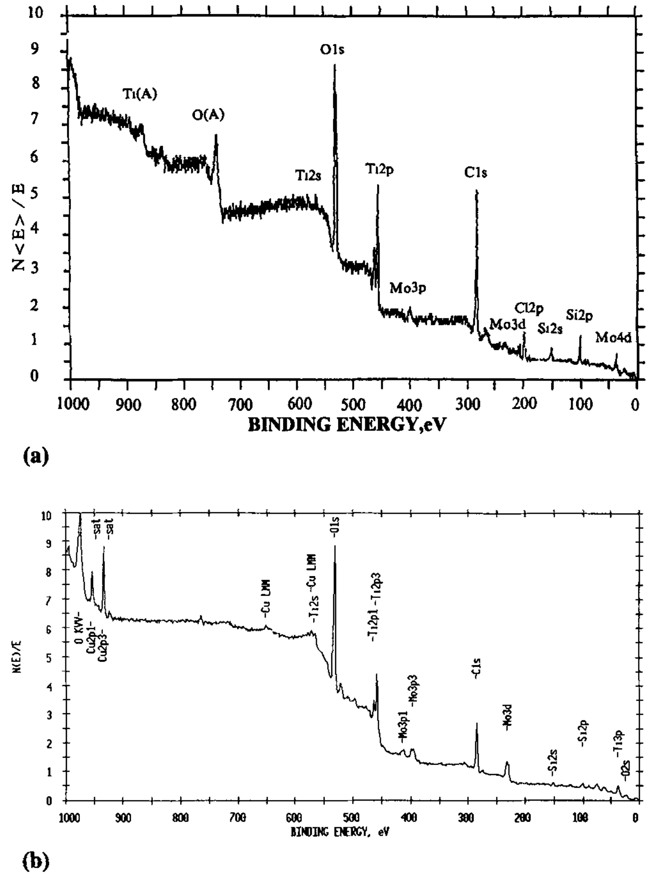

Fig. 2 Typical survey spectra of XPS obtained from the surface of the passive specimens before Ar^+ ion sputtering: (a) at +0.900 V (SCE) for 24 h in 4 mol/L HCl, (b) at –0.600 V (Hg/Hg_2SO_4) for 24 h in 2 mol/L H_2SO_4

minimum content of chloride ion are 15.33 and 2.53 wt%, respectively. The chloride ions are distributed over a great depth of the film. When the content of chloride is 4.6 wt% at the profile depth of 6 nm at +0.900 V in 4 mol/L HCl and the C 1s, Si 2s, and Si 2p peaks have disappeared, the Cl 2p peak is still apparent in the survey spectrum of 6 nm depth (Fig. 3). This result indicates that the higher contents of C and Si in the outer layer of the film are due to the pollution of the surface during the test performance, but that the chloride ions are incorporated into the passive film during its formation. Table 2 shows that very little content of sulfide ion is found in the outer layer of the film of Ti-15Mo alloy in the H_2SO_4 solution at –0.600V (Hg/Hg_2SO_4). The sulfide fraction sharply decreases with the increase of sputtering depth. The content of sulfide is 1.87 wt% at a sputtering depth of 0 nm and is as low as 0.74 wt% at a sputtering depth of 4 nm. It can be inferred that sulfur is not incorporated into the passive film during its formation. A little sulfide contained in the outer layer passive film is due to SO_4^{2-} adsorption on the surface of the passive film. This phenomenon is quite different from that of Ti-15Mo alloy in HCl solution. In Fig. 2(b), the eV values of Ti 2p, Mo 3d, and O 1s peaks show the passive film formed on the Ti-15Mo alloy only consists of titanium-molybdenum oxide in H_2SO_4 solution, in accordance with Wagner et al. (Ref 10). In Fig. 2(a), the eV values of Cl 2p, Ti 2p, Mo 3d, and O 1s peaks indicate the film consists of chloride and oxide of Ti and Mo in HCl solution. Further study is needed to determine whether oxychloride also occurs.

4. Conclusions

- Ti-15Mo alloy has better passivity than pure Ti in HCl and H_2SO_4 solutions. Passivity is related to the enrichment of Mo in the surface of the passive film.
- The anions of the electrolytes influence the composition of the passive film. In HCl solution, chloride ions are incorporated into the passive film during its formation. The passive

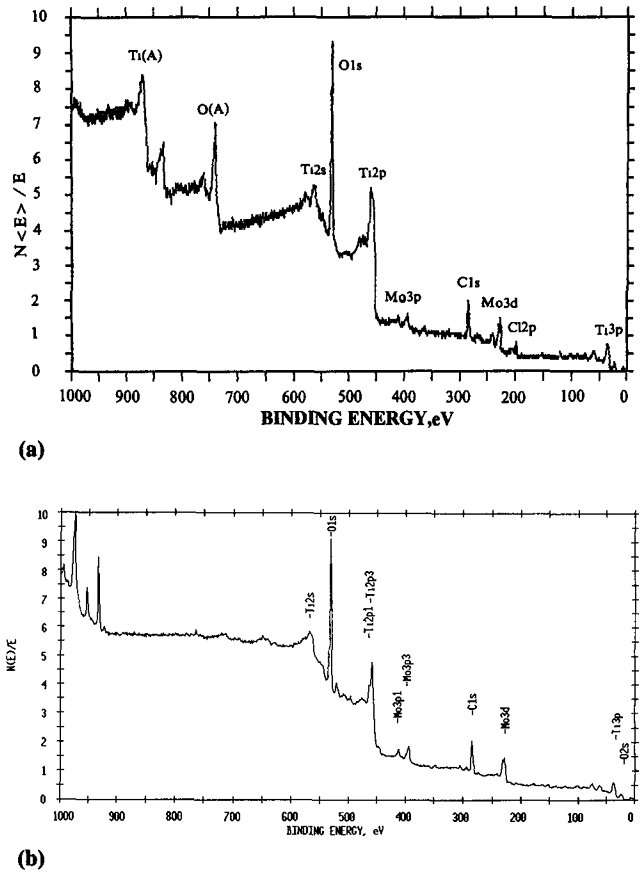

Fig. 3 Survey spectrum of XPS obtained from the passive specimen: (a) in 4 mol/L HCl at +0.900 V (SCE) for 24 h, 6 nm sputtering depth, (b) in 2 mol/L H_2SO_4 at –0.600 V (Hg/ Hg_2SO_4) for 24 h, 4 nm sputtering depth

film consists of chlorides and oxides of Ti and Mo. In H_2SO_4 solution, the passive film consists only of oxide of Ti and Mo; sulfide ions are not incorporated.

- The different anodic polarization potentials have influence on the content of Mo in the film. At lower anodic polarization potentials, the surface of the passive film is enriched in Mo. However, at higher anodic polarization potentials, the surface of the passive film is diluted in Mo.

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