The Anodic Passivity of the Sputter-Deposited W-Ti Alloys in Hydrochloric Solutions

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Abstract
A beneficial effect of titanium in the anodic passivity of the sputter-deposited amorphous or nanocrystalline W-Ti alloys has been studied after immersion or potentiostatic polarization for 1 h in hydrochloric acids at 30°C, open to air by electrochemical measurements and X-ray photoelectron spectroscopy (XPS) analysis. The protectiveness of the anodic passive films formed on the W-Ti alloys is better than that of tungsten. Titanium element acts synergistically with tungsten in enhancing the anodic passivity of the W-Ti alloys. XPS analysis shows that the formation of new anodic passive double oxyhydroxide films composed of W$^{6+}$ and Ti$^{4+}$ ions are responsible for enhancing anodic passivity of the W-Ti alloys. These films have higher protectiveness and stability than those of anodic passive oxyhydroxide films of alloying elements. The anodic polarization at about 0.4 V to 1.2 V (SCE) leads to thickening of the anodic passive films for the W-Ti alloys in hydrochloric acids, mainly due to an increase in hexavalent tungsten in addition to the cations of the alloying elements.

Keywords: Corrosion resistance, Passivity, XPS, Potentiostatic polarization

Introduction
The formation of anodic passive films on alloys has gained great scientific interest for a long time. It is important from a practical point of view that the anodic film causes the passivity. The passivity of metals and alloys mostly concerns the corrosion resistance, and hence the interest is focused on the chemical stability of the anodic passive films.

Several surface studies have been carried out for an understanding of the role of tungsten on the passivity of stainless steels in aggressive chloride media (Naka et al. 1978, Wang & Merz 1984, Habazaki et al. 1991). It has been reported that the addition of tungsten to stainless steel improved the passivity by increasing the stability of the film by the formation of an insoluble tungsten (VI) oxide in acidic-chloride solutions (Bui et al. 1983). Similarly, the addition of tungsten improved remarkably the pitting resistance of aluminum by the formation of a thick hexavalent tungsten oxide in chloride containing acidic solutions (Shaw et al. 1990, Yoshioka et al. 1991).

Recently, a new approach to the roles of alloying elements in the passivation of alloys has been reported by Marcus (1994) which are based on two fundamental properties of metals, namely, the heat of adsorption of oxygen or OH and the heat of sublimation of the metal. Therefore, a subtle balance between these properties of the metal is crucial in the selection of alloying constituents for the binary alloys enhancing passivation. Titanium corresponds to a passivity promoter, and shows such unique properties as a relatively high heat of adsorption of oxygen and a relatively low titanium-titanium bond strength. On the other hand, tungsten is known as the dissolution moderator or blocker with a high heat of adsorption of oxygen and high tungsten-tungsten bond strength. It is, therefore, very interesting to study the role of titanium in the anodic passivity of W-Ti alloy in aggressive environments.

The main objective of this study is to characterize the composition and structure of anodic passive films formed on the sputter-deposited binary W-Ti alloys...
after potentiostatic polarization in 6 and 12 M HCl solutions at 30°C, open to air by XPS analysis.

**Methodology**

Binary W-Ti alloys were prepared by direct current (D. C.) magnetron sputtering on glass plates as described elsewhere (Bhattarai 1998). An electron probe microanalysis (EPMA) was used to determine the composition of the sputter deposits. The structures of the sputter-deposited W-Ti alloys were confirmed as nanocrystalline or amorphous single phase by X-ray diffraction (XRD) with Cu Kα radiation at α-2θ mode.

Prior to immersion tests, electrochemical measurements and XPS analysis, the surface of specimens was polished mechanically with silicon carbide paper to grit 1500 in cyclohexane, rinsed with acetone and dried in air. Open circuit immersion and potentiostatic polarization at several potentials for 1 h were carried out in concentrated hydrochloric acids at 30°C, open to air. A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. All the potentials given in this paper are relative to SCE.

Before and after immersion or potentiostatic polarization, the composition of the surface film and the underlying alloy surface were analyzed by XPS using a Shimadzu ESCA-850 photoelectron spectrometer with Mg Kα excitation (X-ray energy source; Mg Kα, hv = 1253.6 eV). A vacuum of the XPS was maintained about 1-3 x 10⁻⁸ torr during the measurement. The XPS spectra over a wide binding energy region (0-1000 eV) exhibited peaks of carbon, chlorine, oxygen, tungsten and titanium. The most intense peaks of the C Is, C1 2p, O Is, W 4f and Ti 2P₃/₂, electrons were measured in the binding energy range of 20 eV for all the spectra. The binding energies of electrons were calibrated using the method described elsewhere (Asami 1976, Asami & Hashimoto 1977). The binding energies of the Au 4f₇/₂ and 4f₅/₂ electrons of gold metal and Cu 2p₃/₂ and 2p₁/₂ electrons of copper metal were taken as 84.07, 87.74, and 932.53 and 952.35 eV, respectively, and the kinetic energy of the Cu L₂M₄,M₅,₅ Auger electrons of copper as 918.65 eV (Asami 1976). The peak binding energies of each peak were further corrected using the value of the energy of C 1s level (285 eV) for contaminant hydrocarbons. The composition and thickness of the surface films and the composition of the underlying alloy surface were quantitatively determined by a previously proposed method (Asami & Hashimoto 1977) using integrated intensities of photoelectrons under the assumption of a three layer model of the outermost contaminant hydrocarbon layer of uniform thickness, the surface film of uniform thickness and the underlying alloy surface of X-ray photoelectron spectroscopically infinite thickness.

**Results**

**Potentiostatic Polarization Measurements**

Potentiostatic polarization measurements were carried out for binary W-Ti alloys to gain a better understanding of the anodic passivity of the alloys after potentiostatic polarization for 1 h in hydrochloric acids at 30°C. Figures 1 (a) and (b) show changes in anodic current densities of the W-22Ti and W-58Ti alloys, respectively, as a function of polarization time. The anodic current densities of the W-22Ti and W-58Ti alloys in 12 M HCl solution tend to increase initially with polarization time and the current density becomes almost steady after prolonged polarization. The same trend was observed for the W-22Ti and W-58Ti alloys in 6 M HCl at 30°C. This result indicates that initially the dissolution of the W-Ti alloys occurs and then the protective passive film is formed on the W-Ti alloys.

Figure 2 shows potentiostatic polarization curves for W-22Ti and W-58Ti alloys in 6 and 12 M HCl solutions. Some of the present authors have been reported that the current densities of the sputter-deposited tungsten were about 1.5 A/m² and 1.8 A/m² in 6 M (Bhattarai et al. 1995) and 12 M (Bhattarai et al. 1997) HCl solution at 30°C, respectively, and those reported values are higher than those of the W-22Ti
and W-58Ti alloys in both 6 and 12 M HCl solutions as shown in Fig. 2. Furthermore, the anodic current density of the W-58Ti alloy is lower than that of the W-22Ti alloy in both 6 and 12 M HCl. These facts reveal that the protectiveness of the anodic passive films formed on the W-Ti alloys is better than that of tungsten, and the protective quality of the anodic film formed on the W-22Ti alloy containing higher tungsten content is inferior than the W-58Ti alloy. The stability of the passive films seems to be weakened with an increase in HCl concentration, since the anodic passive current density is higher in 12 M HCl than that in 6 M HCl for W-Ti alloys examined in this study.

**Composition of Anodic Passive Film**

The change in the surface composition of the anodic passive films formed on the W-Ti alloy after potentiostatic polarization for 1 h in 6 and 12 M hydrochloric acids at 30°C were analyzed by XPS. Figure 3 shows the cationic fractions in the passive films and the atomic fractions in the underlying alloy surface for the W-22Ti and W-58Ti alloys polarized in 6 and 12 M HCl solutions at 30°C. The cationic fraction in the air-formed film and atomic fraction in the underlying alloy surface after air exposure on mechanically polished alloys are also shown for comparison. Titanium ions are concentrated in the air-formed films on the as-polished specimens. Tungsten is significantly concentrated in both the passive films and underlying alloy surface at the open circuit potential or lower potentials. The enrichment of tungsten decreases by anodic polarization. When the W-22Ti alloy is polarized at high potentials, remarkable tungsten enrichment occurs in the film formed in 6 M HCl, while in 12 M HCl the cationic composition in the film becomes almost the same as the bulk alloy composition, although tungsten enrichment is still maintained the underlying alloy surface.

Figure 4 shows a typical example of the ratio of
[OH⁻]/[cations] and [O²⁻]/[cations] in the passive films formed on W-22Ti and W-58Ti alloys, as a function of potential. The ratios of [OH⁻]/[cations] and [O²⁻]/[cations] in the air-formed film after air exposure on mechanically polished alloy is also shown for comparison. The surface films formed on the tungsten alloys consists of oxyhydroxide in which O²⁻ ion is a major oxygen species. Furthermore, the ratio of [OH⁻]/[cations] is almost independent of potentials, while the ratio of [O²⁻]/[cations] slightly increases with increasing the anodic polarization. Accordingly, the anodic passive films formed on the W-Ti alloys are composed of oxyhydroxides of both tungsten and titanium ions in which O²⁻ ion is remarkably higher than OH⁻ ion.

Anodic Film Thickening And Distribution of Tungsten Ions

The anodic polarization leads to thickening of the anodic passive films formed on the W-Ti alloys in hydrochloric acids. A remarkable anodic film thickening of the sputter-deposited W-Ti alloy is observed at +0.4 V (SCE) or higher potentials. The distribution of both tungsten and titanium cations of the W-Ti alloys in the anodic passive films play an important role in the film thickening of the alloys. Weights of both cations of the W-Ti alloys increase with anodic polarization, although cationic fractions in the anodic films formed on the tungsten alloys is almost constant. Similarly, the change in different oxidation states of tungsten ion in the anodic film greatly affect the film thickening. When W⁴⁺ is oxidized to W⁶⁺ ions by anodic polarization and when W⁶⁺ becomes the main oxidation state of tungsten, a remarkably thick anodic film is formed. Consequently, anodic polarization leads to the anodic film thickening due to increases in W⁶⁺ ions and cations of the alloying element of tungsten-based alloys. Although oxidation of W⁴⁺ to W⁶⁺ becomes remarkable at about 0.1 V (SCE) on tungsten metal (Habazaki et al. 1992), W⁴⁺ ions are stable up to about 0.2 V (SCE) on the tungsten alloys due to protection by the presence of cations of corrosion-resistant alloying elements. Polarization at further higher potential results in sharp increase in the ratio of W⁶⁺ to total tungsten cations in addition to film thickening. Therefore, the effect of cations of titanium and tungsten ions in the anodic film thickening of the W-Ti alloys are discussed in detail.

As shown in Fig. 5, the anodic film thickening for the W-58Ti alloy is almost the same in both 6 and 12 M HCl, while for the W-22Ti alloy a significantly thick anodic film is formed in 6 M HCl than in 12 M HCl after polarization at +0.2 V (SCE) or higher potentials. Figure 6 shows the concentration of tungsten ions for the W-22Ti alloy at +0.2 V (SCE) or higher potentials is significantly higher in 6 M HCl than in 12 M HCl, while the concentration of tungsten ions for the W-58Ti alloy at +0.4 V (SCE) or higher potentials is almost the same in both 6 and 12 M HCl solutions as shown in Fig. 7. On the other hand, as shown in Fig. 8 the amount of W⁶⁺ ions is significantly higher in 6 M HCl than in 12 M HCl for the W-22Ti alloy at the potential regions where a remarkably thick
Change in Binding Energy With Composition of Anodic Passive Films

As shown in Figs 8 and 9, the tetravalent tungsten is the main oxidation state of tungsten for all the tungsten alloys at +0.2 V (SCE) or lower potentials, while the hexavalent tungsten is the main oxidation state of tungsten at +0.4V (SCE) or higher potentials in hydrochloric acids. According to Bhattarai (1998), the anodic film is formed in 6 M HCl. Furthermore, the amount of W⁶⁺ ions is almost the same in both 6 and 12 M HCl for the W-58Ti alloy at the potential regions where a remarkably thick anodic film is formed in 6 and 12 M HCl solutions as shown in Fig. 9. Consequently, remarkably thick anodic film is formed particularly on the W-22Ti alloy in 6 M HCl, because of the formation of relatively high amount of W⁶⁺ ions in 6 M HCl than in 12 M HCl.

Fig. 7. Changes in weights of cations in the surface films formed on the W-58Ti alloy after potentiostatic polarization for 1 h in (a) 6 M and (b) 12 M HCl at 30°C, as a function of potential.

Fig. 8. Changes in weights of W⁴⁺, W⁵⁺ and W⁶⁺ ions in the surface films formed on the W-22Ti alloy after potentiostatic polarization for 1 h in (a) 6 M and (b) 12 M HCl at 30°C, as a function of potential.

Fig. 9. Changes in weights of W⁴⁺, W⁵⁺ and W⁶⁺ ions in the surface films formed on the W-58Ti alloy after potentiostatic polarization for 1 h in (a) 6 M and (b) 12 M HCl at 30°C, as a function of potential.

Fig. 10. Changes in the binding energies of (a) W⁶⁺ 4f⁷/₂ electrons and (b) Ti⁴⁺ 2p⁹/₂ electrons in the anodic passive films formed on the W-Ti alloys after potentiostatic polarization at 1.0 V (SCE) in 12 M HCl, as a function of cationic functions in the film.
tetravalent tungsten and Ti^{4+} ions are located very closely in the films formed on the spontaneously passivated W-Ti alloys so as to show the electronic interaction between W^{4+} and Ti^{4+} ions of the W-Ti alloys. Furthermore, Fig. 10 shows a typical example of the change in the binding energies of core electrons, that is, W^{6+} 4f_{5/2} and Ti^{4+} 2p_{3/2} electrons in the anodic passive films formed on the W-Ti alloys after potentiostatic polarization at 1.0 V (SCE) for 1 h in 12 M HCl, as a function of cationic fractions in the passive film. The binding energy of W^{6+} 4f_{5/2} electrons decreases with the titanium content of the anodic passive film, while that of the Ti^{4+} 2p_{3/2} electrons increases with the tungsten content of the film. This implies that charge transfer occurs from Ti^{4+} to W^{6+} ion and hence tungsten and titanium ions are located very closely in the anodic passive film, so as to show the electronic interaction between W^{6+} and Ti^{4+} ions. The same trend of the electronic interaction between W^{6+} and Ti^{4+} ions was observed in the anodic passive film at 0.4 V (SCE). Accordingly, the anodic passive film on W-Ti alloys is not a heterogeneous mixture of tungsten oxyhydroxide and titanium oxyhydroxide but composed of a double oxyhydroxide consisting of W^{6+} and Ti^{4+} ions. Consequently, the passive films formed on the W-Ti alloys under open circuit condition and at cathodic potentials consist of double oxyhydroxides of W^{4+} and Ti^{4+} ions, and those formed by anodic polarization consist of W^{6+} and Ti^{4+} ions.

Discussion

The passive film composition of the W-Ti alloys changes mainly in three regions, that is, the active regions of titanium, the passive regions of titanium, and the region where oxidation of W^{4+} to W^{6+} occurs. If the W-Ti alloys are polarized near the active potential regions of titanium (that is, at -0.5 to -0.2 V (SCE)) Bhattachari 1998), a significant enrichment of tungsten is observed. Consequently, tungsten is remarkably concentrated in the passive films formed on the W-Ti alloys near the active region of titanium in hydrochloric acids. If tungsten is significantly concentrated in the passive films by the preferential dissolution of titanium ion from air-formed films, tetravalent tungsten is main tungsten species at the open circuit potential. When tetravalent tungsten is oxidized to hexavalent tungsten by anodic polarization, the concentration of tungsten ions slightly decreases with increasing the cationic fraction of titanium in the passive films formed on W-Ti alloys.

Dissolution of the less protective air-formed films in hydrochloric acid at 25°C solution enhanced the formation of more protective passive films formed on the W-Ti alloys. This is mostly due to the formation of passive double oxyhydroxide films composed of both tungsten and titanium cations.

The presence of cations of corrosion-resistant alloying elements increases the stability of W^{4+} ions up to about 0.2 V (SCE), while oxidation of W^{4+} to W^{6+} occurs at about 0.1 V (SCE) on tungsten metal (Habazaki et al 1992). At the same time, anodic polarization leads to film thickening of the W-Ti alloys in concentrated hydrochloric acids at 30°C. Cations of the W-Ti alloys contribute for the anodic film thickening. The main contributor among tungsten ions for the anodic film thickening of the W-Ti alloys is W^{6+} ions, because a relatively stable and sparingly soluble W^{6+} ions increase remarkably in the anodic passive film in the potential region where film thickening is remarkable in hydrochloric acids.

Conclusion

The role of titanium in the passivity of the anodic passive films formed on the sputter-deposited W-Ti alloys has been studied after potentiostatic polarization for 1 h in concentrated hydrochloric acids at 30°C, by electrochemical measurements and XPS analysis. The following conclusion are drawn from the results.

1. Anodic current densities of the W-Ti alloys decrease with addition of titanium.
2. Alloying with corrosion-resistant titanium extends the stable region of W^{4+} ions in the film. W^{4+} ions are stable up to about 0.2 V (SCE) in the passive films on the W-Ti alloys in contrast to the fact that W^{4+} ions are stable at about 0.1 V (SCE) on tungsten metal.
3. Polarization at further higher potential results in a remarkable increase in the ratio of W^{6+} to total tungsten ions along with anodic film thickening.

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