X–ray Photoelectron Spectroscopic Analyses on the Corrosion–Resistant W–Cr–Ni Alloys in 12 M HCl

Jagadeesh Bhattarai
Central Department of Chemistry, Tribhuvan University, GPO Box 2040, Kathmandu, Nepal
E-mail: bhattarai_05@yahoo.com

The high corrosion behavior of the sputter–deposited amorphous or/and nanocrystalline W–Cr–(4–15)Ni alloys was investigated by corrosion tests, electrochemical measurements and X–ray photoelectron spectroscopy (XPS) including angle–resolved measurements in 12 M HCl at 30ºC, open to air. Particular attention was paid to the effects of tungsten, chromium and nickel metals addition on the surface composition of the passive films formed on the ternary alloys which is related to the corrosion–resistant as well as the anodic passivity of the alloys. Corrosion rates of the alloys (~ 0.85–3.00 $\times 10^{-2}$ mm/y) are about four and three orders of magnitude lower than pure chromium and nickel, respectively, and even slightly lower than tungsten metal. Surface analyses by XPS including angle–resolved measurements revealed that the high corrosion resistance of the ternary W–Cr–(4–15)Ni alloys is mostly due to the formation of homogeneous passive oxyhydroxide films consisting of all alloying cations of the alloys. The beneficial effect of the simultaneous addition of chromium and tungsten is based mainly on the synergistic interaction between chromium and tungsten cations in the homogeneous oxyhydroxide passive films to improve the corrosion behavior as well as the passivity of the W–Cr–(4–15)Ni alloys in 12 M HCl.

Key words: W–Cr–Ni alloys, corrosion, passivity, angle–resolved XPS, potentiostatic measurements.

1. INTRODUCTION

XPS has become a very useful tool for corrosion scientists to study the mechanisms of high corrosion resistance and anodic passivity of the alloys during last four decades after a valuable contribution of Kai Siegbhan and co–workers. The XPS techniques including angle–resolved measurements become one of the best surface sensitive techniques for investigating the chemical composition, oxidation states and the electronic information of the alloying elements in the passive films. On the other hand, the surface analyses of the anodic passive films formed on the alloys give crucial information for a better understanding of the effect of alloy–constituting elements in the passivation behavior of the binary or ternary alloys. In recent years, an in–depth distribution measurement of the anodic passive films by angle–resolved XPS technique has become popular. This allows us to examine the formation of homogeneous or heterogeneous surface films formed on the alloys. Non-destructive angle–resolved XPS technique has been used by a number of researchers to gain information about in–depth concentration profiles of the passive films. In principle, the depth information of the passive film depends on the effective escape depth of photoelectrons, which increases with increase in the take–off angle of photoelectrons relative to the surface of the specimen.

The sputter–deposited alloys consisting of either amorphous or nanocrystalline phases are chemically homogeneous, and hence are interesting in the view of passivity and corrosion resistance. Tungsten, chromium and nickel are regarded as effective alloying elements for enhancing the corrosion–resistance and passivity of the sputter–deposited alloys in aggressive environments. It has been reported that 10 at% or less tungsten addition was enough to cause spontaneous passivation of the sputter-deposited W–Cr alloys and they showed higher corrosion resistance than those of tungsten and chromium. It has been also reported that the sputter–deposited amorphous/nanocrystalline W–Ni alloys were passivated spontaneously and showed high corrosion resistance in concentrated hydrochloric acids. The significant improvement of the corrosion resistance of the binary W–Cr alloys and W–Ni alloys was attributed to the formation of double oxyhydroxide passive films of the alloy-constituting elements from the surface sensitive XPS analyses.

On the other hand, the formation of anodic passive films on alloys have gained great scientific interest for long times. It is also important from a practical point of view that the anodic film causes the passivity. Therefore, it is interesting to study the potential dependence of the surface composition of the anodic films formed on the sputter–deposited W–Cr–Ni alloys to clarify the mechanisms of the high corrosion resistance and anodic passivity of the alloys by XPS analyses. In these context, the present work is aimed to clarify the effects of tungsten, chromium and nickel additions in corrosion–resistant and anodic passivation of the amorphous or/and nanocrystalline W–Cr–(4–15)Ni alloys in 12 M HCl at 30ºC using XPS techniques including angle–resolved measurements.

2. EXPERIMENTAL

The sputter–deposited W–18Cr–14Ni, W–42Cr–5Ni and W–63Cr–15Ni alloys were characterized as an
amorphous single-phase having an apparent grain size of about 1.6 nm, and the sputter-deposited W–75Cr–4Ni alloy was composed of the mixture of amorphous and nanocrystalline phases having the apparent grain size of about 10.2 nm from XRD studies using Scherrer’s formula. These alloys were used in this study. Prior to the immersion tests, electrochemical measurements and XPS analyses, the sputter-deposited W–Cr–(4–15)Ni alloy specimens were mechanically polished with a silicon carbide paper up to grit number 1500 in cyclohexane, degreased by acetone and dried in air. The corrosion rate of the alloy was estimated from weight loss after immersion for 168 h in 12 M HCl at 30°C, open to air. Potentiostatic polarization measurement at various potentials for 1 h was carried out. Then the composition of the passive films formed on the alloys was analyzed by XPS including angle–resolved measurements. Platinum mesh and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively.

Before and after immersion or potentiostatic polarization in 12 M HCl, XPS spectra were measured by a Shimadzu ESCA–850 photoelectron spectrometer with MgKα radiation for surface analyses including the in–depth distribution of the species in the surface of the alloys. XPS spectra for the W–Cr–(4–15)Ni alloys over a wide binding energy region (that is, 0–1000 eV) exhibited peaks of tungsten, chromium, nickel, carbon, oxygen and chlorine. The most intense peaks of the W 4f, Cr 2p, Ni 2p, C 1s, O 1s and Cl 2p electrons were measured in the binding energy range of 20 eV for all spectra. The peak shift caused by the charging effect was corrected using the difference the measured binding energy of the contaminant C 1s peak and assumed value of 285.0 eV. For the specimen polarized or immersed in 12 M HCl, a very weak Cl 2p spectrum was detected at an energy peak at 532.3 eV was assigned to OH oxygen. 12,13 The peak shift caused by the charging effect was measured in the binding energy range of 20 eV for all oxygen and chlorine. The most intense peaks of the W 4f, Cr 2p, Ni 2p, C 1s, O 1s and Cl 2p electrons were measured in the binding energy range of 20 eV for all spectra. The peak shift caused by the charging effect was corrected using the difference the measured binding energy of the contaminant C 1s peak and assumed value of 285.0 eV. For the specimen polarized or immersed in 12 M HCl, a very weak Cl 2p spectrum was detected at an energy peak at 532.3 eV was assigned to OH oxygen. 12,13

The spectra from the alloy constituents indicated the presence of the oxidized and metallic species; the former comes from the surface film and the latter from the underlying alloy surface. The measured spectra of W 4f, Cr 2p3/2 and Ni 2p3/2 electrons were separated into Wox and W4f, Cr2p3/2 and Ni2p3/2, respectively. The integrated intensities of the W0 4f, W4+ 4f, Cr0 2p3/2 and Ni0 2p3/2 electrons were separated into W ox and W4+, Cr2+ and Ni2+, respectively. Furthermore, the W0 4f spectrum was consisted of lower and higher binding energy peaks corresponding to W0 4f7/2 and W0 4f5/2 electrons. Similarly, the Wox 4f spectrum was also composed of three doublets of the overlapped spectra of three oxidized species, that is, doublets of Wox 4f7/2 and W4+ 4f5/2; Wox 4f5/2 and W0 4f7/2; and W0 4f5/2 and Wox 4f5/2 electrons. The integrated intensities of the W0 4f, W4+ 4f, Wox 4f, Cr0 2p3/2, Cr3+ 2p3/2, Ni0 2p3/2, Ni2+ 2p3/2, Ni2+ 2p3/2 were obtained by the same method as those described elsewhere.8,10,12,13

The quantitative determination was performed under the assumption of a three–layer model: 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, along with the assumption of homogenous distribution of the constituents in each layer. For angle–resolved XPS, the angle between the specimen surface and the direction of photoelectron to the detector (take–off angle) was changed by using tilted specimen stages. Other XPS measurements were carried out at fixed take–off angle of 60°. The photo–ionization cross–section of the Cr 2p3/2, Ni 2p3/2 and W 4f electrons relative to the O 1s electrons used were 1.7112, 2.3213 and 2.9714, respectively.

3. RESULTS AND DISCUSSION

Figure 1 shows the corrosion rates of the sputter–deposited W–Cr–(4–15)Ni alloys after immersion for 168 h in 12 M HCl at 30°C. Corrosion rates of the sputter–deposited binary W–18Cr, W–75Cr and W–15Ni alloys including pure tungsten, nickel and chromium metals are also shown for comparison.8,10 All the examined W–Cr–(4–15)Ni alloys show about four and three orders of magnitude lower corrosion rate than those of chromium and nickel metal, respectively, and slightly lower corrosion rate than that of tungsten metal. However, the corrosion rates of the W–Cr–(4–15)Ni alloys are slightly increased with increasing the chromium content in the ternary W–Cr–Ni alloys. Consequently, it can be said that both tungsten and chromium improve the corrosion–resistant of the sputter–deposited W–Cr–Ni alloys synergistically. The similar synergistic effect has been reported by the present author for the sputter–deposited W–xCr alloys.7

It is noteworthy to mention here that corrosion rates of the sputter–deposited ternary W–Cr–(4–15)Ni alloys are lower than that of the sputter–deposited binary W–15Ni alloy, and higher than those of the binary W–(18–75)Cr alloys. These results revealed that the addition of chromium to the sputter–deposited binary W–Ni alloys is effective in enhancing the corrosion resistance in 12 M HCl, while a small addition of nickel to the binary W–Cr alloys is not effective to improve the corrosion–resistant properties of the ternary W–Cr–Ni alloys.

Fig.1. Changes in corrosion rates of the sputter–deposited W–xCr–(4–15)Ni alloys after immersion for 168 h in 12 M HCl solution at 30°C.

Alloying Chromium Content / at %

Corrosion Rate / mm. y−1

W-15Ni

W-18Cr

W-14Ni

W-75Cr-4Ni

W-63Cr-15Ni

W-42Cr-5Ni

W-75Cr

W-15Ni

W-18Cr

W-42Cr-5Ni

W-63Cr-15Ni

W-75Cr-4Ni

W-xCr-(4-15)Ni alloys after immersion for 168 h in 12 M HCl solution at 30°C
The surface analyses of the passive films formed on the W–Cr–Ni alloys using XPS including angle-resolved measurements give important information for a better understanding of the effects of tungsten, chromium and nickel additions in the passivity and corrosion-resistant properties of the alloys. An information about in-depth composition change of the passive film formed on the sputter-deposited W–Cr–Ni alloys was obtained by a non-destructive depth profiling technique of angle-resolved XPS to know whether the passive films formed on the alloys are homogeneous or not.

The changes in the cationic fractions in the passive film and atomic fractions in the underlying alloy surface for the amorphous W–63Cr–15Ni alloy after immersion for 5 h in 12 M HCl at 30°C, as a function of take-off angle of photoelectrons, are shown in Fig. 2. Figure 2 (a) clearly reveals that tungsten is significantly concentrated in the spontaneously passivated films with a significant deficiency of nickel, while a slight deficiency of chromium is also observed. It can, therefore, be said that a significant concentration of tungsten is necessary for maintaining the spontaneous passivation of the sputter-deposited W–63Cr–15Ni alloy, because nickel and chromium are active in 12 M HCl. Furthermore, the chromium content in the passive film is slightly lower than that of the bulk alloy composition. However, the concentration of chromium is slightly higher in the exterior part (at take-off angle of 30°) and the tungsten content is slightly higher in the interior part (at take-off angle of 90°) of the tungsten-rich passive film formed on the W–63Cr–15Ni alloy by immersion for 5 h in 12 M HCl at 30°C, while there is no clear concentration gradient of nickel content in-depth of the passive film formed on the alloy. On the other hand, tungsten and nickel are generally concentrated with the deficiency of chromium content in the underlying alloy surface as shown in Fig. 2(b). Accordingly, it can be said that all cations of the W–63Cr–15Ni alloy are distributed homogeneously in the passive film formed on the spontaneously passivated alloy in 12 M HCl, although there is a very small concentration gradient of chromium and tungsten cations.

In general, one of the characteristic of the surface film is the concentration of oxygen species. Figure 3 shows the changes in the ratios of \([O^2–]/[\text{cations}]\) and \([\text{OH}–]/[\text{cations}]\) in the passive films formed on the W–63Cr–15Ni alloy in 12 M HCl, as a function of take-off angle of photoelectrons. The ratios of \([O^2–]/[\text{cations}]\) increase with take-off angle and the ratios of \([\text{OH}–]/[\text{cations}]\) decrease with take-off angle. Consequently, the interior part of the passive film formed on the W–63Cr–15Ni alloy is rather dry and well developed by M–O–M bridging while the exterior part of the passive film is slightly wet with OH– ions. In general, the concentration ratios of \(O^2–\) and \(OH–\) ions are greater than unity in the surface films formed on the sputter-deposited ternary W–Cr–Ni alloys. Consequently, the passive films of the W–Cr–Ni alloys are composed of oxyhydroxides in which \(O^2–\) ions are significantly higher than \(OH–\) ions.

Electrochemical measurements were carried out for better understanding of the high corrosion resistance of the W–Cr–(4–15)Ni alloys. Figure 4 shows the potentiostatic polarization curves for the W–Cr–Ni alloys after polarization for 1 h in 12 M HCl at 30°C, open to air. All the examined W–Cr–Ni alloys are spontaneously passivated in wide polarization potentials until the transpassive dissolution of chromium occurs. The anodic current densities of the alloys decrease with increasing the chromium content. Accordingly, the protective quality of the anodic passive films formed on the W–63Cr–15Ni alloy after immersion for 5 h in 12 M HCl at 30°C, as a function of take-off angle.
properties of the W–Cr–Ni alloys, and such a beneficial effect is not observed with a small addition of nickel in the alloys as observed in Fig. 1.

The changes in the surface composition of the anodic passive films formed on the spontaneously passivated W–Cr–Ni alloys after potentiostatic polarization were analyzed by XPS. Figures 5, 6 and 7 show the cationic fractions in the surface films and atomic fractions in the underlying alloy surface on W–18Cr–14Ni, W–63Cr–15Ni and W–75Cr–4Ni alloys, respectively, after potentiostatic polarization for 1 h in 12 M HCl at 30°C. The cationic fractions in the air-formed film and atomic fractions in the underlying alloy surface after mechanical polishing (that is, as-polished) are also shown for comparison. The enrichment of tungsten ions (W$_{\text{ox}}$) with deficient of chromium ion (Cr$_{3+}$) is clearly observed in the passive films formed on the W–18Cr–14Ni and W–63Cr–15Ni alloys at the corrosion potential ($E_{\text{corr}}$) and cathodic polarization potentials, while anodic polarization leads to an increase in Cr$_{3+}$ ion with decreasing the W$_{\text{ox}}$ ions in the passive films formed on the W–18Cr–14Ni and W–63Cr–15Ni alloys, and hence the cationic fractions of Cr$_{3+}$ ion exceeds the alloy compositions of both. Furthermore, a significant deficiency of nickel ion (Ni$_{2+}$) is clearly observed for all the examined alloys in this study. On the other hand, the enrichment of Cr$_{3+}$ ion with deficient of both W$_{\text{ox}}$ and Ni$_{2+}$ ions is clearly observed in the passive film formed on the W–75Cr–4Ni alloy even at more noble cathodic polarization potentials, corrosion potential ($E_{\text{corr}}$) and anodic polarization potentials, and hence the cationic fractions of the Cr$_{3+}$ ion exceeds the alloy composition as shown in Fig. 7. These results revealed that the passive film composition of the W–Cr–(4–15)Ni alloys changes mainly in three regions, that is, active, passive and transpassive regions of the alloying elements. Consequently, the tungsten ions are remarkably concentrated in the passive films formed on the alloys near the active regions of chromium and nickel in 12 M HCl solution at 30°C. However, the chromium content in the passive film is remarkably concentrated when the alloys are polarized in the passive potential regions of chromium (that is, between –0.1 and 0.8 V (SCE)) in 12 M HCl. At higher anodic potentials, the cationic fractions of chromium ion is decreased near the transpassive region of chromium as a result of oxidation of Cr$_{3+}$ to Cr$_{6+}$, because Cr$_{6+}$ ions dissolve easily into 12 M HCl solution. Consequently, when the ternary W–Cr–Ni alloys are polarized near the transpassive potential regions of chromium metal (that is, more than about +0.8 V SCE), the concentration of W$_{\text{ox}}$ ion is slightly increased with decreasing chromium content in the anodic passive film.
In general, the chromium content of the underlying alloy surface is slightly increased with anodic polarization potentials, while the nickel content of the underlying alloy surface is slightly decreased. In addition, tungsten content in the underlying alloy surface is almost same as that of the bulk alloy composition.

The anodic polarization leads to thickening of the anodic passive films formed on the W–Cr–(4–15)Ni alloys in 12 M HCl at 30°C as shown in Fig. 8. In general, remarkable anodic film thickening is clearly observed at +0.2 V (SCE) or higher potentials. It is noteworthy that the thicker passive films are formed on the W–Cr–Ni alloys containing higher amounts of tungsten ions than those of the alloys containing lower amounts of tungsten ions in all anodic polarization potentials. Consequently, the film thicknesses of both the W–63Cr–15Ni and W–75Cr–4Ni alloys are almost same for all the polarization potentials, and are thinner than that of the anodic passive film formed on the W–18Cr–14Ni alloy. These results revealed that the distribution of tungsten and chromium cations of the ternary W–(18–75)Cr–(4–15)Ni alloys in the anodic passive films play an important role in the film thickening of the W–Cr–Ni alloys in 12 M HCl at 30°C. In particular, changes in different oxidation states of tungsten ions in the anodic passive film greatly affect the film thickening.

Figures 9(a) and 9(b) show the ratios of W^{4+}, W^{5+} and W^{6+} ions in the films formed on the W–18Cr–14Ni and W–75Cr–4Ni alloys, respectively, as a function of potential. When W^{6+} is oxidized to W_{O2}^{4+} ions by anodic polarization and W_{O2}^{4+} 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 increase in W_{O2}^{4+} ions of the ternary W–Cr–Ni alloys. Although oxidation of W_{O2}^{4+} to W_{O2}^{5+} becomes remarkable at about 0.1 V (SCE) on pure tungsten metal, W_{O2}^{5+} ion is stable up to about 0.2 V (SCE) on the W–Cr–(4–15)Ni alloys due to protection by the presence of cations of the alloying elements. Polarization at further higher potential results in sharp increase in the ratio of W_{O2}^{6+} ion to the total tungsten cations in addition to anodic film thickening.

Figures 10(a) and 10(b) show changes in the ratios of [O^{2-}]/[cations] and [OH^{-}]/[cations] in the films formed on the W–18Cr–14Ni (a) & W–75Cr–4Ni alloys after polarization for 1 h in 12 M HCl at 30°C, as a function of potential.

Figures 10(a) and 10(b) show changes in the ratios of [O^{2-}]/[cations] and [OH^{-}]/[cations] in the films formed on the W–18Cr–14Ni and W–75Cr–4Ni alloys,
respectively, as a function of potential. As mentioned in Fig. 3, the spontaneously passivated films formed on the W–Cr–Ni alloys consist of oxyhydroxide in which O$^{2-}$ ion is a major oxygen species. Furthermore, the ratios of [OH]/[cations] is almost independent of potential, while the ratios of [O$^{2-}$]/[cations] slightly increase with increasing the anodic polarization. Accordingly, the anodic passive films formed on the W–(18–75)Cr–(4–15)Ni alloys are composed of oxyhydroxides of cations of alloying elements in which O$^{2-}$ ion is remarkably higher than OH$^-$ ion similar to the films formed on the spontaneously passivated ternary W–Cr–Ni alloys in 12 M HCl at 30°C, open to air.

4. CONCLUSIONS
The mechanism of the synergistic effect of chromium and tungsten elements enhancing the higher corrosion resistance and passivity of the sputter-deposited amorphous or an nanocrystalline W–Cr–(4–15)Ni alloys than those of alloy–constituting elements has been studied by immersion tests, electrochemical measurements and XPS including angle–resolved measurements in 12 M HCl at 30°C, open to air.

ACKNOWLEDGEMENTS
The author is very thankful to Professor Emeritus Dr. Koji Hashimoto of Tohoku Institute of Technology and Professor Emeritus Dr. K. Asami of Institute for Materials Research of Tohoku University, Sendai, Japan for their kind permission to use the XPS machine for surface analyses.

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(Received August 27, 2009; Accepted January 6, 2010)