Study on the synergism of corrosion-resistant W-xNb alloys by angle-resolved X-ray photoelectron spectroscopy

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Highlights

- Use of AR-XPS method for in-depth analysis of sputter-deposited binary W-base alloys with Nb.
- Corroding processes of the W-base deposits containing 26 and 78 at % Nb were studied in 12 M HCl.
- Uniform distribution of W^{ox} and Nb^{5+} occurs in the alloy films in very aggressive media.
- A homogeneous film is needed for showing synergistic corrosion-resistant properties of alloys.

RESEARCH ARTICLE

Study on the synergism of corrosion-resistant W-xNb alloys by angle-resolved X-ray photoelectron spectroscopy

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Abstract: The synergistic effect of simultaneous addition of tungsten and niobium to the sputter-deposited binary alloys of W-xNb ($x = 26, 78$) on exhibiting a very high corrosion-resistant activity in 12 M hydrochloric acid was studied using depth profiling technique of an angle-resolved X-ray photoelectron spectroscopy (AR-XPS) at 30 °C. Both binary W-26Nb and W-78Nb alloys exhibited higher corrosion resistance properties compared with those of alloying metals, tungsten and niobium. The average corrosion rate (0.0054 - 0.0101 mm/y) noticed was nearly ten times less compared with that of W and Nb metals. Results of the depth profiling analyses of these corrosion-resistant W-xNb alloys by AR-XPS technique revealed that such corrosion action of the alloys is largely owing to the occurrence of homogeneous passive layers with W^{ox} and Nb^{5+} ions without in-depth concentration variations after immersion in 12 M hydrochloric acid, open to air, at 30 °C. As a consequence, W and Nb metals acted synergistically in increasing the spontaneous passivity and the high corrosion resistance of the W-xNb deposits in 12 M hydrochloric acid.

Keywords: Angle-resolved XPS; corrosion-resistant; in-depth analysis; sputter-deposition; tungsten alloys.

INTRODUCTION

A non-destructive AR-XPS has been extensively used by several scientists for characterizing the in-depth concentration profiles of a thin film (Bare *et al.*, 2016) because it has various advantages over several destructive surface analysis techniques (Demchenko *et al.*, 2018). Mostly the AR-XPS demonstrates a promising depth profiling examination of the distribution of the elements in different depth layers of a thin film to look into constituent elements, chemical, electronic (Alba *et al.*, 2020), magnetic (Ciocarlan *et al.*, 2020), and surface-sensitive (Hernandez *et al.*, 2017) properties of the films formed on any solid substrates. It has been demonstrated that the AR-XPS allows for investigating surface processes, even at gas-liquid as well as the liquid-solid interfaces in a recent development (Niedermaier *et al.*, 2016). The surface sensitivity of XPS cannot be varied by angle-resolved studies because of the particulate micro-geometry of the sample, and hence any changes in elemental concentration with distance from the surface would have to be deduced from the AR-XPS studies on smooth solid surfaces (Sakamoto *et al.*, 2020).

The AR-XPS technique becomes one of the very viable tools to reason out the causes of showing synergistic corrosion mechanism by the metastable sputter deposits containing two or more elements during the last three decades (Park *et al.*, 1996; Bhattarai *et al.*, 1997, 1998a; Li *et al.*, 1998). In particular, tungsten-based alloys have shown synergistic properties of lower corrosion rate than those of all elements of the binary and ternary alloy deposits in very corrosive media (Bhattarai and Kharel, 2009; Sah and Bhattarai, 2009; Kharel *et al.*, 2013). Besides, an XPS fast depth profiling technique has been recently developed to study the stainless steel oxide layer structure (Detriche *et al.*, 2020). Moreover, the results of recent AR-XPS studies of the native oxide films formed on titanium-based binary alloys containing more than 40 wt.% showed excellent corrosion performance in an aerated Hank's solution, mostly due to the homogeneous distribution of Ta_2O_5 in the top-most layer of the alloy surface (Mendis *et al.*, 2020). It was investigated an air exposure effect on the passivity of a steel electrode in glutarate solution, and the results gave evidence that passivity was favored by progressively hydroxylated native oxide films from the AR-XPS analysis though the film disclosed the bilayer structures (Chan-Rosado and Pech-Canul, 2019).

Niobium and tungsten metals are believed as efficient alloying elements for making corrosion-resistant alloys (Chen *et al.*, 2017). Previous studies give detailed efforts for successfully preparing a single-phase amorphous/nanocrystalline W-based (Bhattarai, 2002; Aryal and Bhattarai, 2010; Baral and Bhattarai, 2014; Khadka and Bhattarai, 2014), and Nb-based (Leinartas *et al.*, 2015) deposits using the technique of sputtering. These binary alloys were reported to be spontaneously passive and they showed a low corrosion rate in offensive environments even though they showed a lower corrosion rate than one of alloying elements of all the alloys. It was generally observed before the 1990s that the corrosion rates of the binary alloys were decreased with the addition of comparatively more corrosion-resistant elements, and it reached almost near (but not exceed) the corrosion value of the high corrosion-resistant element of the alloy (Hashimoto *et al.*, 1998). However, during the 1990s, the most interesting fact was reported that the corrosive level of some sputter deposits like Cr-Nb (Li *et al.*, 1998), W-Ti

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(Bhattacharai *et al.*, 1995), W-Ta (Bhattacharai *et al.*, 1998b) and W-Nb (Bhattacharai *et al.*, 1998c) alloys showed lower corrosion rates compared with their respective alloying elements in very reactive environments. In particular, the sputter deposits W-xNb with amorphous and nanocrystalline structures demonstrated the synergistic corrosion lowering effect with lower corrosive properties than unalloyed W and Nb metals in aggressive hydrochloric acids (Bhattacharai *et al.*, 1998d), and neutral and alkaline electrolytes (Jha and Bhattacharai, 2008).

Furthermore, niobium and its alloys are also extensively used in machine parts with anti-corrosion properties in industrial sectors where the system runs in aggressive environments (Aimone and Yang, 2018). The corrosion properties of a series of Nb-Ti alloys were examined which was remarkably improved in artificial human fluids with recorded a few $\mu\text{A}/\text{cm}^2$ corrosion current densities (Vishnu *et al.*, 2019). Besides, there is a tendency to develop titanium-based binary and ternary alloys containing remarkable amounts of niobium which have high biocompatibility, corrosion-resistant, and mechanical properties close to that of human bone (Karre *et al.*, 2015). About 2 - 15 at.% addition of Nb did not have noteworthy effects on the general corrosion rate of the sintered Ti-Ni alloys, but significantly improved the localized corrosion resistance and the passivity (Lethabane *et al.*, 2015) in artificial saliva and 0.9% NaCl solution, respectively. Besides, tungsten-based oxides showed meritorious properties of electro-catalytic and corrosion-resistant properties (Kusmierek, 2021). However, these tungsten- and niobium-based alloys, mostly prepared within the last two decades have not studied their surface properties using the in-depth surface analysis methods.

In such circumstances, it was focused to clarify the facts behind showing high anti-corrosion properties of the W-26Nb and W-78Nb deposits compared with pure W and Nb deposits in very reactive hydrochloric acid solution at room temperature using the surface-sensitive depth-profiling technique of AR-XPS. The findings of the recent studies of the compositional depth profiling of the thin films formed on binary W-xNb deposits could be insightful and good suggestive in reasoning out the synergistically higher corrosion-resistant behavior of all the binary and ternary alloys than those of their alloying elements even in very reactive media. This would be perceptive in describing such types of synergistic anti-corrosion properties of all the binary and ternary alloy deposits.

MATERIALS AND METHODS

The W-based two deposits containing 26, and 78 atomic percentage (at.%) niobium were prepared on glass substrate using DC sputtering machine. For this purpose, 99.95% pure tungsten and niobium disks having 100 mm and 6 mm diameters, respectively, were used as described elsewhere (Bhattacharai, 1998). The W-26Nb deposit with 26 nm apparent size and W-78Nb deposit with 1.6 nm were identified as nanocrystalline and amorphous structures, respectively, from XRD data. Before the immersion tests, and AR-XPS analyses, both alloys were mechanically polished using a

SiC paper (No. 1500) in cyclohexane, degreased by acetone (Rana *et al.*, 2017), and dried to remove the surface oxides of the alloys through its atmospheric oxidation during storage. Three specimens with known areas of each alloy were immersed for one week in 12 M HCl at 30 °C, open to air, and then recorded their mass lost values, separately. The recorded mass lost value of each alloy specimen was used to estimate the average corrosion rate (CR) using the relation given as; $\text{CR (mm/yr)} = [8.76 \times 10^4 \times \text{mass lost (g)}] / [\text{density (g/cm}^3) \times \text{area (cm}^2) \times \text{time (h)}]$, described elsewhere (Subedi *et al.*, 2019).

The in-depth compositional variation in both the tungsten-based niobium alloys was analyzed by AR-XPS. For this purpose, an electron spectrometer (Shimadzu ESCA-850, Japan) was used with an X-ray source of MgK_{α} rays, as described elsewhere (Bhattacharai, 2021). The XPS spectra peaks of W, Nb, C, O, and Cl for the W-xNb ($X = 26, 78$) deposits were firstly recorded between 0 - 1000 eV binding energy (BE) regions, and then the XPS spectra of W 4f, Nb 3d, O 1s, C 1s, and Cl 2p electron states were recorded in 20 eV BE range. A feeblest Cl 2p peak at about 199.0 eV was recorded among these XPS peaks because each alloy specimen that was exposed to HCl, was washed several times using deionized water. Hence, the chloride concentration was not considered in the quantitative analyses. The C 1s XPS peak value of 285.0 eV was used as a correction factor for the XPS peak shifting due to the charging effects, as recommended elsewhere (Greczynski and Hultman, 2020).

Five different take-off angles (TOA) of photoelectron (*i.e.*, 30°, 45°, 60° and 90°) were adjusted using tilted-specimen holders for the depth profiling AR-XPS analysis, as discussed elsewhere (Sakhonenkov *et al.*, 2019). The symbols of oxidized ($^{\circ}$) and metallic ($^{\circ}$) species which come from the passive layers and underlying alloy surface of the W-xNb deposits are used hereafter. The W° 4f spectrum, which is furthermore, separated into W^{4+} 4f, W^{5+} 4f, and W^{6+} 4f spectra. The recorded W 4f and Nb 3d electron spectra were split up into W° 4f and W° 4f, and Nb^{5+} 3d and Nb° 3d spectra which are depicted in Figure 1, for the nano-crystal structure of the W-26Nb deposits in the given conditions. Moreover, the W° 4f and Nb° 3d spectra have separated a pair of spectra for both (*i.e.*, W° 4f $_{7/2}$, W° 4f $_{5/2}$ electrons, and Nb^{5+} 3d $_{5/2}$, Nb^{5+} 3d $_{3/2}$ electron, respectively). Furthermore, the W° 4f spectrum was separated into three pairs of doublets (W^{4+} 4f $_{7/2}$ and W^{4+} 4f $_{5/2}$; W^{5+} 4f $_{7/2}$, and W^{5+} 4f $_{5/2}$; W^{6+} 4f $_{7/2}$, and W^{6+} 4f $_{5/2}$ electrons). In the same manner, the Nb^{5+} 3d spectrum has consisted of a pair of Nb^{5+} 3d $_{5/2}$ and Nb^{5+} 3d $_{3/2}$ electrons which is also demonstrated in Figure 1. The integrated intensities of the W° 4f, W^{4+} 4f, W^{5+} 4f, W^{6+} 4f, Nb° 3d, and Nb^{5+} 3d were calculated using the photo-ionization cross-section values of 2.97 (Kawashima *et al.*, 1984) for W 4f electrons, and 2.981 (Hirota *et al.*, 1991) for Nb 3d electrons, as explained elsewhere (Bhattacharai *et al.*, 1998c).

Besides, the separation of OM and OH oxygen from the O 1s spectrum was done, as demonstrated in Figure 1. The OH oxygen spectrum was further separated into OH $^-$ and adsorbed H_2O molecules for the quantitative analysis.

Figure 1: Quantitative XPS analysis model for W-xNb alloys (Bhattarai, 1998).

All these integrated intensities of both the anion and cation species present in the W-xNb deposits were used for the in-depth compositional variation of the alloy using three layers (*i.e.*, bulk alloy, alloy surface and surface film) model, as depicted above in Figure 1.

RESULTS AND DISCUSSION

The mass loss of three specimens of each alloy including W and Nb metals was estimated for the calculation of average CR which is shown in Figure 2. The average CRs of both the W and Nb deposits were 0.0276 mm/y and 0.0310 mm/y, respectively, in 12 M HCl at 30 °C. Besides, the W-26Nb and W-78Nb deposits showed the corrosion rate of 0.0054 mm/y and 0.0101 mm/y, respectively, which is even lower than those of W and Nb metals. In particular, the corrosion resistance of the W-26Nb deposit is found to be about one order of magnitude higher than pure W and Nb metals in such reactive electrolytes. Accordingly, simultaneous additions of both W and Nb metals in the W-26Nb and W-78Nb deposits improved the corrosion resistance synergistically. Similar results of W-yNb ($y = 7 - 70$ at %) alloy deposits were previously reported in hydrochloric

acid solutions (Bhattarai *et al.*, 1998c). In particular, the corrosion-resistance properties of the tungsten-rich W-Nb alloys containing 7 - 45 at % Nb were lower in 6 M HCl than 12 M HCl solution, whereas the corrosion resistance properties of the alloys with 45 - 70 at.% Nb were reported higher in 12 M HCl than in 6 M HCl (Bhattarai *et al.*, 1998d).

Such an anomalous behavior of the binary W-Nb alloys in HCl solutions was explained by the surface analysis using conventional XPS and atomic force microscopic (AFM) techniques (Bhattarai *et al.*, 1998d). In particular, the conventional XPS analysis clarified that such synergistic improvement of the anti-corrosion properties and anodic passivity of these W-xNb deposits were mainly based on the formation of more protective and diffusion-barrier oxyhydroxide anodic layers with W (VI) and Nb (V) ions which were not formed on the surfaces of pure W and Nb metals in 12 M HCl at 30 °C (Bhattarai, 2011). In another research work, it was reported that the additions of 13-92 at % Nb in W showed synergistic anti-corrosion properties showing higher corrosion-resistant (~ 10 times) than that of alloying W in neutral NaCl and NaOH solutions, and it was even lower than that of Nb metals (Jha and Bhattarai, 2008). However, the causes of such synergistic corrosive nature of the W-Nb deposits regarding the in-depth compositional distribution of all anions and cations contained in the thin film were not studied using the AR-XPS technique. In this regard, the causes of showing such synergistic consequences of W and Nb additions for anti-corrosion properties of two W-xNb ($x = 26$ and 78 at.%) alloys were aimed to clarify from AR-XPS analysis.

Figure 2: Estimated corrosion rates of W, Nb and W-xNb ($x = 26$ and 78) deposits.

Figure 3 illustrates the quantitative outcomes of the in-depth variations in apparent fractions of the W^{ox} and Nb^{5+} in passive surface layers, and the fractions of W and Nb metals in the alloy surfaces of both the W-xNb ($x = 26, 78$) deposits as a function of TOA in the given conditions. The W^{ox} is notably enriched in the spontaneously passivated and alloy layers of both alloy deposits with a substantial deficiency of niobium ions due to its dissolution in 12 M HCl, as depicted clearly in Figure 3.

Figure 3: Changes of the apparent cationic and atomic fractions in surfaces formed on the W-26Nb and W-78Nb alloys, as a function of TOA.

Furthermore, no change of concentration of each W^{ox} or Nb^{5+} ion in different depths of the spontaneously passivated surfaces of both the corrosion-resistant W-xNb deposits exposed in H^+ ion-containing solution for 5 h. However, there is a small concentration gradient of the W and Nb cations in the alloy (underlying) surfaces. Tungsten is slightly concentrated in the interior part of the underlying surface of the niobium-rich W-78Nb deposit. Accordingly, it could be said that W^{ox} and Nb^{5+} are distributed without any concentration variation in the passive thin layer of the sputter-deposited tungsten-based binary alloys containing 26 and 78 at.% Nb after exposure for 5 h in 12 M hydrochloric acid at 30 °C.

The AR-XPS measurements disclosed that the passive films without concentration variation of W^{ox} and Nb^{5+} ions in passive are responsible for showing synergistically high corrosion resistance of the W-xNb alloy even in chloride-containing 12 M hydrochloric acid solution. Consequently, the W-xNb deposits exhibited higher corrosion resistance than those of the pure W and Nb metals in aggressive hydrochloric acid solution at 30 °C. Based on such AR-XPS results, a model was proposed to represent the distribution of both cations (W^{ox} and Nb^{5+}) in W-xNb alloys, as presented schematically in Figure 4. There are no gradients of W^{ox} and Nb^{5+} amounts in-depth of the less corrodible passive layers.

It was also reported in the previous studies that the oxygen affinity of niobium was found to be higher than the tungsten in the W-Nb alloys when exposed to atmospheric air, although the niobium oxide on the air-formed film was reported to dissolve more remarkably than that of tungsten oxides after exposing 5 hours or more of the W-Nb alloys in 12 M HCl solution (Bhattacharai *et al.*, 1998c). The similar type of the synergistic effects of higher corrosion resistance behavior of the sputter-deposited binary amorphous or nano-crystalline binary and ternary tungsten-based (Bhattacharai, 2012), aluminum-based

Figure 4: A model of the uniform passive and underlying surfaces formed on the W-xNb deposits.

(Akiyama *et al.*, 1996), chromium-based (Li *et al.*, 1998), and molybdenum-based (Park *et al.*, 1996) alloys than their respective alloying elements were reported in aggressive electrolytes, mostly due to the homogeneous films formed on the alloys from AR-XPS analysis. It was reported that there were no concentration differences of W^{ox} and Ti^{4+} ions in in-depth of the thin passive and underlying layers of the W-xTi alloy deposits after their exposure for one day or more in 12 M hydrochloric acid solution at 30 °C (Bhattacharai, 2020).

To a similar degree, the AR-XPS analysis indicated that the concentrations of Nb(V) and Cr(III) ions were uniformly distributed in different depths of the passive films of the chromium-rich binary niobium-based alloy deposits in very acidic solutions which might be the main responsible reason for showing such high corrosion resistance properties even in such aggressive electrolytes at 30 °C (Li *et al.*, 1998). A similar result was reported for sputter deposits of Mo-Nb alloys in the very reactive concentration of HCl (Park, 1996). These alloys exhibited extremely high corrosion resistance properties, mostly due to the development of a spontaneously passivated film formed on the alloy surface in which in-depth distributions of all ions were found to be homogeneous from the AR-XPS studies. From the above observations and discussion, it could be summarized that the non-destructive composition depth profiling analysis by AR-XPS would be discerning and perceptive to explain the synergistic anti-corrosion properties exhibited by binary and ternary sputter deposits in very corrosive electrolytes.

Moreover, changes in the ratios of different oxidized species of W (W^{4+} , W^{5+} and W^{6+}) in the less active and diffusion-barrier passive layer formed on the W-Nb deposits were assessed quantitatively for knowing an advantageous influence of oxidized tungsten role in the in-depth proofing study of the passive layers of the deposits. Figure 5 demonstrates the quantitative ratios of the W^{4+} , W^{5+} and W^{6+} ions in the passive layers of the W-26Nb alloy

Figure 5: Relative amounts of W^{4+} , W^{5+} and W^{6+} ions in the passive layers of W-26Nb deposit after exposure in 12 M HCl for 5 h at 30 °C as a function TOA.

deposit as the referred condition. The figure clearly showed that the relative ratio of W^{4+} species increases with TOA, while a reverse trend was observed in the distribution of the relative ratio of W^{6+} in the passive layers. In contrast, the relative ratio of W^{5+} species remains almost constant with TOA. These observations cleared that W^{4+} species are present mostly in the interior part of the passive layers, and W^{6+} species are more abundant in the exterior of the passive

layers. The same trend of the depth profiling distribution of W^{4+} , W^{5+} and W^{6+} species in the passive layers formed on the synergistic corrosion-resistant W-25Cr (Bhattarai, 2021), W-22Ti (Bhattarai, 2020), W-32Zr (Bhattarai, 2014), W-23Ta (Bhattarai, 2012) and chromium-rich W-63Cr-15Ni (Bhattarai, 2010) sputter deposits.

Likewise, amounts of oxygen species distributed in the passive layers of the corrosion-resistant alloy deposits are generally of three types; O^{2-} , OH^- , and adsorbed H_2O species, and sometimes both OH^- and adsorbed H_2O species are collectively accounted as OH. Figures 6(a), 6(b), 6(c) and 6(d) demonstrate the changes of the XPS peak intensities of the oxygen species measured for the W-26Nb deposit at 15°, 30°, 60° and 90°, respectively, after exposure the deposit in 12 M HCl solution for about 5 h, open to the air, at 30 °C. The figures demonstrate that the relative amounts of OH^- species should be higher than O^{2-} at low TOA (example, at 15 °), while its amounts decrease with increasing the O^{2-} species with increasing the TOAs between 30° and 90°, as depicted in Figure 6. Consequently, it is assumed that the interior of the passive layers of the W-32Nb deposit is well matured with relatively dry M–O–M bridging, while the exterior passive layers are slightly wet with more amounts of OH^- ion and H_2O which might be one of the reasons for showing significantly more anti-corrosion properties of the W-xNb deposits than those of their constituting elements in such aggressive electrolyte of 12 M HCl solution. The identical results of the depth profiling distribution of oxygen species in the layers of Nb and its alloys (Wang, 2014), other multi-component films (Lubchenko *et al.*, 2018) were reported in the literature.

Figure 6: Deconvoluted O 1s spectra for W-26Nb deposit at (a) 15°, (b) 30°, (c) 60° and (d) 90° of TOA (θ).

CONCLUSION

Showing the synergistic anti-corrosion properties of W and Nb by the W-26Nb, and W-78Nb deposits in very aggressive 12 M HCl solution at 30 °C are proved to be mostly due to the formation of dry and well-developed diffusion barrier in passive layers consisting of W^{ox} and Nb⁵⁺ ions without any concentration gradient in in-depth of the layers. However, the concentrations of the tetravalent tungsten and O²⁻ species are especially concentrated in the interior of the passive layers formed on W-26Nb and W-78Nb deposits. The in-depth compositional analysis by AR-XPS technique could be insightful and suggestive to explain all types of synergistic properties including corrosion-resistant, mechanical, electronic, and so on shown by different binary or ternary alloys.

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DECLARATION OF CONFLICT OF INTEREST

The author declares that there is no conflict of interest.

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