# An XPS and AFM study of Ar<sup>+</sup>-ion-etched Ni–W alloy surfaces prepared by DC magnetron sputtering

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Institute of Chemistry of Center for Physical Sciences and Technology, A. Goštauto 9, LT-01108 Vilnius, Lithuania The surface of Ni–W alloy coatings deposited by direct-current (DC) reactive magnetron sputtering before and after annealing was examined by X-ray photoelectron spectroscopy (XPS) and with the atomic force microscope (AFM). The XPS depth profiles of as-deposited Ni–W alloys with a different content of W (25, 50 and 75 at.%) show the compositional and chemical shifts indicating an obvious increase of W content in all sputtering depth due to preferential Ni sputtering. The binding energy (BE) of Ni2p3 peaks increases with increasing the tungsten content in the alloy, while the binding energy of W4f7 peaks decreases with decreasing the nickel content; this reflects the well-known alloying effect on the chemical shifts. The heating (T = 850 °C in H<sub>2</sub>) of as-sputtered Ni–W alloys shows that W is preferentially oxidized and causes the crystalline structure and a remarkable coarsening of alloy surfaces.

Key words: Ni-W alloys, heat treatment, XPS, AFM, Ar+ ion etching

## INTRODUCTION

The process of sputter removal of atoms from surfaces has become a very important adjunct to technological analysis of surface chemistry, using X-ray photoelectron spectroscopy (XPS) and sometimes Auger electron spectroscopy (AES) [1]. In the field of surface chemistry, including corrosion and annealing studies, XPS gives extremely useful characteristics for studying the nature of surface films and their substrate. The mechanism by which chemical effects may occur in two-component targets due to ion sputtering is not well understood [2]. Ion bombardment is used to obtain direct information on the depth distribution of elements (depth profiles), because this etching technique is especially sensitive in the nearsurface region, i. e. less than several nm. Usually, the atomic layers of the target surface are considered to be sputtered layer by layer under ion bombardment without a significant disturbance of the distribution or chemical state of elements in the target surface [3, 4]. However, there are some studies to show that ion bombardment can influence the target surface by the ways of preferential sputtering (PS), radiation-induced segregation (RIS) and the bombardment-enhanced Gibbsian segregation (GS) [5–8]. It is proposed that these influences bring about compositional changes at the surface or nearsurface area of the target, especially in oxide films of metals [2, 5, 9]. Therefore, ion etching seems to be a more complex process, and the XPS data must be interpreted cautiously. The XPS technique should be able to give some insight into this problem under  $Ar^+$  ion etching conditions, provided it does not change the chemical state of the specimen under analysis. Compositional depth profiles have become a routine part of the analysis of surface layers in microelectronics [10–12], corrosion science [13] and a host of other areas, such as ion beam etching (or thinning) of thin film specimens for examination in a transmission electron microscope (TEM) [8].

The alloys of the iron-group metals have been widely applied in industry, mainly as materials for magnetic storage devices and electronics. Due to their hardness, they can successfully substitute hard chromium coatings which are formed in an environmentally hazardous process based on hexavalent chromium. Investigations of Donten et al. [14] have shown that among amorphous alloys with tungsten, Ni–W was of the best smoothness and appearance; however, it poorly adheres to steel substrates and has a high internal stress. Tungsten heavy alloys are two-phase composites consisting of nearly pure tungsten grains dispersed in a low melting temperature ductile matrix of other metals such as Ni, Fe, Cu and Co [15–17]. These alloys offer a unique combi-

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nation of properties associated with the bcc tungsten phase and the fcc matrix, such as higher mechanical properties and good corrosion resistance. Ternary W–Ni–Fe alloys may exhibit the key properties of the Fe–W and Ni–W alloys while eliminating the unwanted properties of the two-component alloys, so they are important materials leading to many practical applications [18, 19]. The necessary amount of passivating elements in the alloys often cannot be acquired by equilibrium processing or electrodeposition; thus, recent efforts in the preparation of new corrosion-resistant alloys have mostly involved the use of sputter-deposition technique which is suitable for the formation of a single-phase solid solution [20].

In this paper, we report an analysis of the surface composition of Ni–W alloy coatings prepared by the DC magnetron sputtering deposition method and measurements of  $Ar^+$ ion depth profiling, studied by the XPS and AFM methods. Moreover, the aim of the present work was to ascertain what additional information the depth profiling yields when the depth profiles before and after heat treatment were compared.

## EXPERIMENTAL

#### Deposition

The direct-current (DC) reactive magnetron sputtering in the UNIVEX 350 deposition system was applied to obtain Ni–W alloys. The base chamber pressure was typically below  $1.5 \times 10^{-4}$  Pa, and the Ar working gas pressure was  $2.0 \times 10^{-1}$  Pa. The substrates used for each deposition were Ø 15 mm steel (AISI) discs which were polished and finished with a diamond paste of 1 µm until the mirror outlook was obtained. The substrate holder with four wafers symmetrically opposing each other was rotated at a speed of 18 rev/min to maximize the thickness and compositional uniformity of coatings. Before sputtering, the holder with wafers was heated to 72 °C under the base chamber pressure, and the growing temperature was maintained at 60 °C. The deposition time for Ni–W alloy with different content (in at. %) of Ni and W was 60 min. The power applied to the Ni target was 74 W and 121 W, and the tungsten target was, respectively, 92 W and 52 W. After deposition, for two specimens (  $Ni_{50}W_{50}$  and  $Ni_{75}W_{25}$ ) a 2-h annealing at 850 °C was carried out in a conventional furnace under a flow of Cu boring purified hydrogen (purity 99.995%) atmosphere to avoid oxidation.

#### XPS and AFM measurements

XPS measurements were performed with a Vacuum Generator (VG) ESCALAB MKII spectrometer to analyze the chemical state of elements on Ni–W alloy surfaces before and after annealing. The non-monochromatic Al K $\alpha$  X-ray radiation (hv = 1486.6 eV) was used for excitation. The Al twin anode was powered at 14 kV and 20 mA.The photoelectron takeoff angle with respect to the sample surface normal was 90°, and XP spectra of Ni2p, W4f, O1s, Fe2p and C1s were taken at a constant analyzer energy mode (at 20 eV pass energy). The base pressure in the working chamber was kept bellow  $5 \times 10^{-7}$  Pa. The spectrometer was calibrated relative to  $Ag3d_{5/2}$  at 368.0 ± 0.1 eV and  $Au4f_{7/2}$  at 83.8 ± 0.1 eV. For sputter etching, the argon gas pressure was maintained at  $6 \times 10^{-3}$  Pa, and the Ar+ ion gun was operated at 4 keV and 100  $\mu$ A at an angle of ~60°. The operation of depth profiling consisted of the repetition of the sputter etching for 2, 4, 8 and 16 min, followed by XPS measurement until the total sputtering period reached 24 min. The quantitative elemental analysis was done by estimating peak areas and taking into account empirical sensitivity factors for each element [21]. A standard program was used for data processing (XPS spectra were treated by a Shirley-type background subtraction and fitted with mixed Gaussian-Lorentzian functions). Binding energies (BE) were referenced to the C1s (284.5 eV) on unsputtered surfaces.

The surfaces of Ni–W alloys, as-deposited and after annealing before and after depth profiling, were examined with an atomic force microscope (AFM) on an Explorer scanning probe (ThermoMicroscopes, USA) at atmospheric pressure and room temperature in contact mode. For average roughness measurements, data were derived from  $5 \times 5 \ \mu\text{m}^2$  surface images obtained by AFM. The roughness of the polished steel substrates was 0.0 nm before Ni–W alloy DC magnetron sputtering.

#### **RESULTS AND DISCUSSION**

The XPS depth profiles of as-deposited Ni-W alloys with different content of W (25, 50 and 75 at. %) show notable compositional and modest chemical shift deviations when the analysis is extended to the alloy substrate (until the Fe2p3 peak emerges). These data are presented in Table 1 in which one can see that the Ni / W atomic ratio in these films changes slightly as a function of the sputtering time, indicating that the composition of alloys has remained uniform during Ar<sup>+</sup> ion bombardment. As predicted by the stoichiometry formula of  $\mathrm{Ni}_{25}\mathrm{W}_{75},\mathrm{Ni}_{50}\mathrm{W}_{50}$  and  $\mathrm{Ni}_{75}\mathrm{W}_{25}$  alloys, their ratio must be 0.33, 1 and 3, respectively, but in all sputtering depth the Ni / W ratio was always lower compared with that of the stoichiometric composition. Under steady-state conditions, tungsten concentration of ~76.9 at. % for  $Ni_{25}W_{75}$ , ~52.8 at. % for  $Ni_{50}W_{50}$ and ~28.0 at. % for  $Ni_{75}W_{25}$  was measured at the surface region, showing an obvious enrichment in W content. The pure element sputtering yields  $(Y_{Ni} / Y_{W} = 1.3)$  [2] indicated that, besides Ni preferential sputtering, also other processes, such as contaminations and oxidation on the target surface, affect the composition of the altered layer. The difference between the measured and the stoichiometric ratios is related to the preferential sputtering of nickel during the Ar<sup>+</sup> ion etching of the Ni-W alloy surface. In fact, when a multi-elemental material is bombarded, the lighter element (nickel) is sputtered preferentially as compared with a heavier element (tungsten)

Compound	Sputtering time (min)	Ni / W ratio	Ni BE (eV)	W BE (eV)
Ni <sub>25</sub> W <sub>75</sub>	2	0.26	852.9 ± 0.1	$31.0\pm0.1$
	8	0.3	852.7 ± 0.1	$31.0\pm0.1$
	16	0.26	852.7 ± 0.1	$30.9\pm0.1$
	24	0.26	852.7 ± 0.1	$31.0\pm0.1$
Ni <sub>50</sub> W <sub>50</sub>	2	0.89	$852.9 \pm 0.1$	$31.2\pm0.1$
	8	0.86	$852.9 \pm 0.1$	$31.0\pm0.1$
	16	0.76	$852.9 \pm 0.1$	$30.9\pm0.1$
	24	0.80	$852.9 \pm 0.1$	$30.9\pm0.1$
Ni <sub>75</sub> W <sub>25</sub>	2	2.29	852.7 ± 0.1	31.1 ± 0.1
	8	2.3	852.7 ± 0.1	31.1 ± 0.1
	16	2.4	852.7 ± 0.1	31.1 ± 0.1
	24	2.6	852.7 ± 0.1	31.1 ± 0.1

Table 1. The sputter time, Ni / W ratio and binding energy values determined for as-deposited N–W films

[5, 7, 24]. J. Bartella and H. Oechsner investigated the stoichiometric variations of a polycrystalline Ni 79.2–Mo 20.8 alloy induced by normal bombardment with Ar<sup>+</sup> ions (of 40 to 2000 eV) using Auger electron spectroscopy and have found that the depth profiles display a pronounced enrichment of Mo content in the etched surface region [25].

In binary Ni–W alloys, the binding energy of Ni2p3 peaks increases with the tungsten content in the alloy, while the binding energy of W4f7 peaks decreases with decreasing the nickel content in the alloy (Table 1). This is a well-known alloying effect on the chemical shifts [26] due to rearrangment of the electronic orbital in bonding with nickel and reveals the charge transfer from nickel to tungsten.

According to the literature, electrodeposited Ni-W coatings containing 25 at. % W and more form a nano-crystalline Ni<sub>4</sub>W and amorphous phases which are transformed to NiW (1:1) during annealing [27–29]. Furthermore, the authors of [27, 29] have reported-after X-ray diffraction (XRD) pattern inspections that an increase in W content leads to a substantial peak broadening which is quantified through the trend of a decreasing grain size and also is consistent with lattice swelling due to a relatively large size of W atoms in Ni-W solid solution. In our experiment, the deposition time of sputtered Ni-W films was selected so that the final thickness in the range of 0.5-1 µm could be obtained. Thus, no XRD technique was employed to characterize these alloys. The AFM was selected due to its capability to determine the surface topography and the height map over a given area in a fairly large height scale. The average surface roughness, Rq (nm), of DC magnetron sputtered Ni–W alloys with a different content of W (25 and 50 at. %) after Ar<sup>+</sup> ion etching and heat treatment is summarized in Table 2. An increase in W content resulted in a reduced surface roughness of as-deposited alloys. Ar<sup>+</sup> ion etching for 24 min significantly influenced the development of surface roughness of both alloys: it increased the roughness for Ni<sub>50</sub>W<sub>50</sub> and decreased for Ni<sub>75</sub>W<sub>25</sub>.

As indicated in Fig. 1 (a and c), the AFM images of asdeposited  $Ni_{50}W_{50}$  and  $Ni_{75}W_{25}$  alloys showed a relatively smooth surface with randomly distributed nodules and exhibited a microcrystalline structure with height variations from ~8 to ~16 nm, respectively. Its surface structure during Ar<sup>+</sup> ion etching did not change (Fig. 1, b and d). A similar variation in grain size with changing W content for electrodeposited Ni–W alloys has been reported by many authors [27–31].

As is shown in Fig. 2 (a–d), the XPS Ni2p3 and W 4f corelevel spectra are the same as that of as-deposited  $Ni_{50}W_{50}$ (1 : 1) or  $Ni_{75}W_{25}$  (3 : 1) alloys, suggesting that the damage inflicted by incident Ar<sup>+</sup> ions did not alter the coatings significantly. The relatively high content of carbon and oxygen (not shown) at the sample surface was probably due to contaminations caused by their preparation routine. The BE of Ni2p3 (852.9 eV–852.8 eV) and W4f7 (30.8e V–31.1 eV) spectra differ from their reference values of 852.6 eV and 31.3 eV, respectively, but remain invaried with depth. These chemical shifts can be considered to arise from charge transfer between Ni and W atoms [32].

Table 2. Average surface roughness Rq (nm) of Ni–W alloys with different content of W after various treatments, calculated from AFM images (scan area  $5 \times 5 \mu^2$ )

Sample of Ni—W alloy	Rq, nm
Ni <sub>50</sub> W <sub>50</sub> , as deposited	8.02
$Ni_{50}W_{50}$ , after Ar <sup>+</sup> ion etching (24 min)	11.74
$Ni_{50}W_{50}$ , after heat treatment at 850 °C, 2 h in $H_2$	145.01
$Ni_{s0}W_{s0'}$ after heat treatment and Ar <sup>+</sup> ion etching (24 min)	127.42
Ni <sub>75</sub> W <sub>25</sub> , as deposited	15.67
Ni <sub>75</sub> W <sub>25</sub> , after Ar <sup>+</sup> ion etching (24 min)	9.43
$\rm Ni_{75}W_{25}$ , after heat treatment at 850 °C, 2 h in H <sub>2</sub>	383.43
$Ni_{75}W_{25}$ , after heat treatment and Ar <sup>+</sup> ion etching (24 min)	24.56



**Fig. 1.** AFM images of the surface of Ni–W alloys: (a)  $Ni_{50}W_{50}$  alloy as deposited and (b) the same after etching with Ar<sup>+</sup> ions for 24 min; (c)  $Ni_{75}W_{25}$  alloy as deposited and (d) the same after etching with Ar<sup>+</sup> ions for 24 min



**Fig. 2.** XPS core-level spectra of as- deposited Ni–W alloys and after etching with 5 keV Ar<sup>+</sup> ions for 24 min: a) Ni2p3 spectra and b) W4f spectra of Ni<sub>50</sub>W<sub>50</sub> alloy; c) Ni2p3 spectra and d) W4f spectra of Ni<sub>75</sub>W<sub>25</sub> alloy



**Fig. 3.** XPS core-level spectra of W4f for  $Ni_{50}W_{50}$  (a) and  $Ni_{75}W_{25}$  (b) alloys during Ar<sup>+</sup> ions etching after heat treatment at 850 °C, 2 h in H<sub>2</sub>

The heating of as-sputtered Ni<sub>50</sub>W<sub>50</sub> and Ni<sub>75</sub>W<sub>25</sub> alloys for studying the thermal stability of their structure was carried out at the same temperature (850 °C) in H<sub>2</sub> atmosphere to avoid air oxidation, and then also the depth profile was taken. According to XPS analysis, the surface of these samples was composed of tungsten, oxygen, iron and contaminant carbon, but no evident signal of nickel was checked. Further, a comparison of the W4f core-level peaks in Fig. 3 (a and b) for both alloys shows that annealing drastically changed the chemical environment of the surface W atoms. Owing to the higher affinity of W to oxygen in comparison to Ni ( $\Delta H_{e}$  $^{NiO} = -241 \text{ kJ} \cdot \text{mol}^{-1}, \Delta H_c^{WO3} = -842.87 \text{ kJ} \cdot \text{mol}^{-1}), W \text{ is prefer-}^{-1}$ entially oxidized [33]. Initially, in the depth profiles, the W4f peaks exist at 35.1 eV on the surface of Ni<sub>50</sub>W<sub>50</sub> and at 35.0 eV on the surface of Ni75W25, which corresponds to tungsten in WO<sub>2</sub> or FeWO<sub>4</sub> state [21, 22]. After starting the etching of Ar<sup>+</sup> ions, the W4f7 peaks have two BE positions at 31.2-35.5 eV for Ni<sub>50</sub>W<sub>50</sub>, and 31.1-35.5 eV for Ni<sub>75</sub>W<sub>25</sub>, indicating metallic W<sup>0</sup> and oxidized state W<sup>6+</sup> of tungsten [21]. The further surface etching of these alloys (up to complete removal) leads to the detection of a weak signal of nickel (not shown) with about 0.5 and 1.6 at. %, respectively, which demonstrates an inward diffusion of Ni into the substrate, whereas about 20–35 at. % Fe was outwardly transported during annealing from the steel substrates.

In the Ni–W system, at high temperatures Ni atoms diffuse three-four times faster than W atoms due to their low mobility, and the diffusion rate of both elements decreases with increasing W content [34]. This explains our observation why such a low content of W was found in the annealed alloys during depth profiling. These data are summarized in Table 3 which reflects actual compositional changes. Lauro et al. [35] have pointed out that the synergetic effect of both nickel and nitrogen is very important in avoiding the inter-diffusion of sputtered tungsten-based coatings and substrate elements, improving also their oxidation resistance.

Figure 4 shows the morphological and structural changes of Ni–W alloys under heat treatment (T = 850 °C, 2 h, H<sub>2</sub>) (4a, 4c) and after etching Ar<sup>+</sup> ions for 24 min (4b, 4d). One can see a clearly crystalline structure and a remarkable coarsening of both alloy surfaces with a very high average roughness of 145 nm and 383 nm for Ni<sub>50</sub>W<sub>50</sub> and Ni<sub>75</sub>W<sub>25</sub>, respectively. The

Compound	Sputtering time (min)	Fe/W ratio	Ni BE (eV)	W BE (eV)	Fe BE (eV)
Ni <sub>50</sub> W <sub>50</sub>	0	1.16	-	35.1	709.5 / 711.9
	2	1.09	852.6 ± 0.1	31.2 / 35.5	706.8 / 708.7
	8	1.16	852.6 ± 0.1	31.2 / 35.5	706.7 / 708.5
	16	1.2	$852.7 \pm 0.1$	31.2 / 35.5	706.7 / 708.7
	24	1.19	852.7±0.1	31.2 / 35.5	706.7 / 708.5
Ni <sub>75</sub> W <sub>25</sub>	0	2	-	35.0	709.8 / 712.2
	2	2.42	852.9 ± 0.1	31.1 / 35.5	706.7 / 708.2
	8	2.58	$852.8 \pm 0.1$	31.0 / 35.5	706.6 / 708.4
	16	2.06	852.9 ± 0.1	31.1 / 35.4	706.6 / 708.4
	24	2.14	852.8 ± 0.1	31.1 / 35.4	706.6 / 708.3

Table 3. DC magnetron sputtered Ni–W films annealed at T = 850 °C for 2 h in H, atmosphere



**Fig. 4.** AFM images of Ni–W alloys and after heat treatment at 850 °C for 2 h in  $H_2$  atmosphere: (a) Ni<sub>50</sub> $W_{50}$  alloy and (b) after its etching with 5 keV Ar<sup>+</sup> ions for 24 min; (c) Ni<sub>70</sub> $W_{50}$  alloy and (d) after its etching with Ar<sup>+</sup> ions for 24 min;

Ar<sup>+</sup> ion etching does not alter significantly the surface of alloys until the steel substrate is reached.

As mentioned in [36], the extent of bombardmentinduced morphology depends primarily on the substrate material, whereas the ion beam characteristics play only a secondary role. Due to the complexity of and the numerous processes involved in ion / solid interactions, the bombardment-induced topography is not well understood. Several quantitative and qualitative theories have been proposed to explain the experimental data. Most of these theories are based on SEM or TEM data. The major disadvantage of these data is the lack of quantitative information. The advent of SPM (scanning probe microscopy) and the subsequent development of software have reversed this disadvantage.

## CONCLUSIONS

The surfaces as deposited by DC reactive magnetron sputtering and after the annealing of Ni–W alloy coatings were examined by XPS and AFM. The XPS depth profiles of asdeposited Ni–W alloys with a different content of W (25, 50 and 75 at.%) indicate an obvious enrichment in W at all sputtering depths due to preferential Ni sputtering. Their surface structure after Ar<sup>+</sup> ion etching, as observed in AFM images, showed no changes and exhibited a microcrystalline structure with height variations from ~8 to ~16 nm. The BE of Ni2p3 peaks increased with the tungsten content in the alloy, while the BE of W4f7 peaks decreased with decreasing the nickel content in the alloy, but remained unchanged as regards the depth. This reflectd the well-known alloying effect on BE shifts.

The annealing of Ni–W alloys (at T = 850 °C, 2 h,  $H_2$ ) demonstrates an inward diffusion of Ni into the substrate and an outward diffusion of Fe (~20–35 at. %) from steel substrate due to the three-fourfold lower mobility of W atoms. Moreover, the heat treatment caused a crystalline structure and coarsening of alloy surfaces with a very high average roughness (145–383 nm). The Ar<sup>+</sup> ion etching does not alter significantly the surface of alloys.

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# AR⁺ JONAIS ĖSDINTŲ Ni−W LYDINIŲ, UŽDULKINTŲ MAGNETRONINIU BŪDU, PAVIRŠIŲ TYRIMAS RFES IR AJM METODAIS

#### Santrauka

Pastovios srovės režime magnetroniškai uždulkinti Ni–W lydiniai ir po jų atkaitinimo buvo ištirti Rentgeno fotoelektroninės spektroskopijos (RFES) metodu ir atominės jėgos mikroskopu (AJM). Tik ką uždulkintų Ni–W lydinių su skirtingais W kiekiais (25, 50 ir 75 at. %) RFES gylio profiliai parodė žymius elementinės sudėties ir nedidelius ryšio energijų cheminių poslinkių nuokrypius, reiškiančius akivaizdų W kiekio padidėjimą visuose ėsdinimo gyliuose dėl greitesnio Ni išėsdinimo. Ni2p<sub>3</sub> pikų ryšio energijų reikšmės padidėja didėjant W kiekiui lydinyje, tuo tarpu W4f<sub>7</sub> pikų ryšio energijų reikšmės mažėja, mažėjant Ni kiekiui lydinyje, atspindėdamos gerai žinomą metalų lydymosi poveikį grynų metalų ryšio energijų cheminiams poslinkiams. Ni–W lydinių atkaitinimas (T = 850 °C, 2 h H<sub>2</sub> atmosferoje) sukėlė vyraujančią W oksidaciją lydinių paviršiuje ir akivaizdų kristalinės struktūros susidarymą bei lydinių paviršiaus šiurkštėjimą.