

STUDY OF THE INITIAL OXIDATION OF THE U₄Zr₂Nb ALLOY BY X-RAY PHOTOELECTRON SPECTROSCOPY

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ABSTRACT

In this work, the initial stages of oxidation of the U₄Zr₂Nb alloy in O₂ atmosphere were studied in-situ, in ultrahigh vacuum, by X-ray photoelectron spectroscopy (XPS), an advanced surface-sensitive technique. After several hours of Ar⁺ ion-sputtering to surface cleanness, the O₂ exposures was realized on the sample at room temperature. The evolution of oxide film formed on the sample surface was followed by XPS measures, by using Mg K_α radiation of 1253.6 eV and a CLAM-2 (Vacuum Generator) electron energy analyzer. The changes of U 4f, Nb 3d, Zr 3d and O 1s photoemission peaks with O₂ exposure indicate that the adsorption of oxygen on the U₄Zr₂Nb alloy surface leads to fast formation of UO₂. The alloying elements show slower oxidation and different compounds are observed in Nb 3d spectra analysis. This work shows an expressive enlargement of Nb 3d peak at 100 Langmuir exposure, indicating the formation of Nb₂O₅ and NbO in the oxide. On the other hand, the binding energy of Zr 3d suggests that the ZrO₂ formation is stable as well as uranium dioxide.

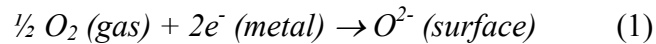
1. INTRODUCTION

Uranium alloys are important materials for applications where a high density of fissile and fertile elements is required. The most common elements added to uranium are niobium, titanium, zirconium, vanadium and molybdenum. These elements are well known for stabilize the uranium gamma fase and, as a consequence, improve the mechanical properties of the resulting alloy, which are necessary for applications as nuclear fuel materials. The presence of the alloying elements are also important to increase the corrosion resistance of the resulted material [1-5]. Among the binary U alloys, the U6Nb and the U10Mo are the ones that seem to present the better resistance against degradation in oxygen-rich environments [1,6]. Among the ternary alloys, the U-Zr-Nb family has been strongly considered in oxidation studies [1]. In these alloys, the Nb can be used to obtain an increase in the ductibility and the Zr is added to increase the chemical compatibility between the fuel and its matrix [1,7].

Despite the known effect of alloying elements in the corrosion, a better understanding of the protection mechanism in these alloys has been possible only lately due to the use of new surface analysis techniques [3,5,8]. Recent studies indicate two mechanisms of oxidation

resistance: one in which the oxidation resistance is related to the formation of an oxide layer rich in noble elements dissolved, and another, where the formation of a mixed oxide layer reduces the diffusion of oxygen ions through the oxide layer [3,5,9].

Previous results about the oxidation mechanism of binary alloys containing Nb indicate that the oxide grown on the alloy surface has remarkable concentration of Nb₂O₅ [5,9]. This oxide is considered as a barrier to oxidation due to its dielectric characteristic that is important in the growth of the oxide since it inhibits the electron transport from the metal to the oxide/gas interface in order to decrease the classical oxidation reactions, such as [10]:



To the best of our knowledge, there are few informations in the open literature about the oxidation mechanism of ternary U alloys containing Nb [1,7], though it is important to study the influence of the combination of different alloying elements in the behavior of the resulting alloy in respect to oxidation. Taking into account the technological importance of the U-Zr-Nb alloys, we carry out a study on the initial oxidation of U4wt%Zr2wt%Nb by X-ray photoelectron spectroscopy (XPS). XPS is a surface sensitive technique, i. e., a technique that allows to access detailed information about the chemistry of the very first monolayers of the surface of a material. Our results point out the oxides formed in this process and may contribute to broaden our knowledge about the oxidation mechanism of this alloy.

2. EXPERIMENTAL

The experiments were performed in an ultrahigh vacuum (UHV) system with base pressure around 7.0×10^{-10} mbar. The XPS measurements data were obtained using a standard non-monochromatic Mg K α X-ray source ($h\nu = 1253.6$ eV) and the photoemitted electrons were detected with a hemispherical concentric analyzer (CLAM2, VG Microtech). The binding energy scale was calibrated using the carbon from the surface contamination found before the sputtering procedure (C 1s at 285.0 eV).

The sample of U4Zr2Nb alloy was prepared for mounting into the UHV chamber by mechanical polishing with a sandpaper 600 grade to remove all surface oxide. Prior the exposure to O₂, the sample surface was sputter-cleaned with a 1.5 keV beam of Ar⁺ ions until the O 1s and C 1s peaks disappear in the XPS measurements. O₂ (99.9999%) exposures were carried out at room temperature and at a pressure of 1.0×10^{-6} mbar. All exposures were measured in Langmuir units (1 L = 1.33×10^{-6} mbar.s). All spectra were taken immediately after sputtering was finished, or gas exposure was completed.

3. RESULTS AND DISCUSSION

Wide XPS spectra before and after exposure to 100 L O₂ are presented in Figure 1. The clean surface, where only the U, Nb and Zr peaks are observed, is shown in Figure 1(a), while the O peak is evident in Figure 1(b). Besides the oxygen presence, the changes in binding energies of the main peaks of the elements can be observed. These energy shifts are better resolved in the detailed spectra for the different exposures.

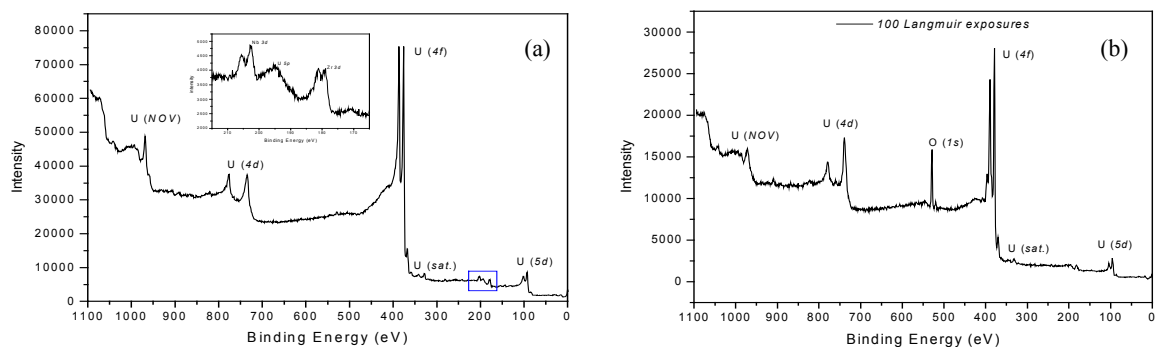


Figure 1 - XP spectra presenting the clean U-Zr-Nb surface after sputtering (a), and the changes after 100 L O₂ (b).

The detailed U 4f spectra before and after the indicated exposures are presented in Figure 2. The U 4f_{7/2} and U 4f_{5/2} peaks are situated at 377.1 and 387.9 eV respectively, before the exposures. After the first exposure (4 L), a new pair of peaks is observed at 380.3 and 390.9 eV, respectively. Followed oxygen exposures it is observed the increase of this peak and another pair of low intensity peaks is observed at 386.7 and 397.2 eV at 25 L. These last ones are the shake up satellite peaks that are features of the U⁴⁺. The presence of these shake up situated at approximately 7.0 eV of the main peak and the shift noted is enough to indicate the formation of stoichiometric UO₂ on the surface [3,5,9].

In order to characterize the compound formed by Zr we analyse the Zr 3d_{5/2} binding energy shift. Before the exposures, the peak is centred at 178.8 eV that is typical to metallic Zr. After the exposures it is observed an increase of a component at 182.5 eV, which overlaps the Zr 3d_{3/2} component of the metallic state. For a better understanding, a line is presented in the Figure 3 as a guide to the eyes to show the peak shift. The peak at 182.5 eV was found in the literature [11] in similar position of the ZrO₂ which seems the more probable oxide formed considering the thermodynamics conditions of the experiment.

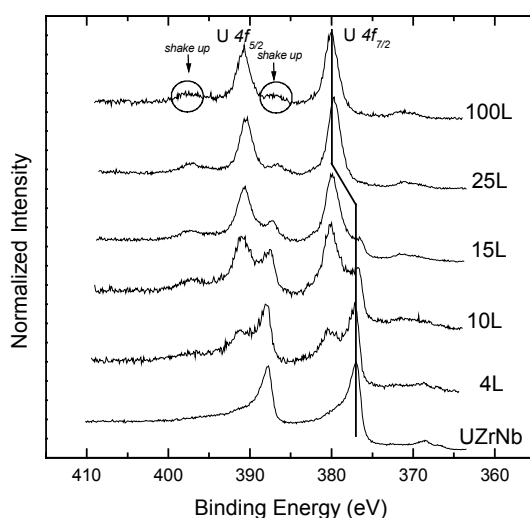


Figure 2. Detailed U4f spectra before and after exposures. It is indicated the UO₂ formation due to the typical binding energy presented and the shake up satellite.

Figure 3 also presents the peak Nb 3d_{5/2} situated at 202.2 eV, before the initial O₂ exposure, which confirms the metallic Nb, also observed in the U2.5Nb by Jiangrong et al. work [5]. As noticed by Manner et al. [3], apparently, alloying uranium with niobium does not change the environment of either metal significantly, as judged from insignificant core level shift. After the exposures the changes perceived in the Nb 3d peak are remarkable and complex; but we can note that the higher intensity of the peak changes to approximately 207.2 eV at 100 L. This binding energy suggests the formation of Nb₂O₅ on the sample surface [5,9,11].

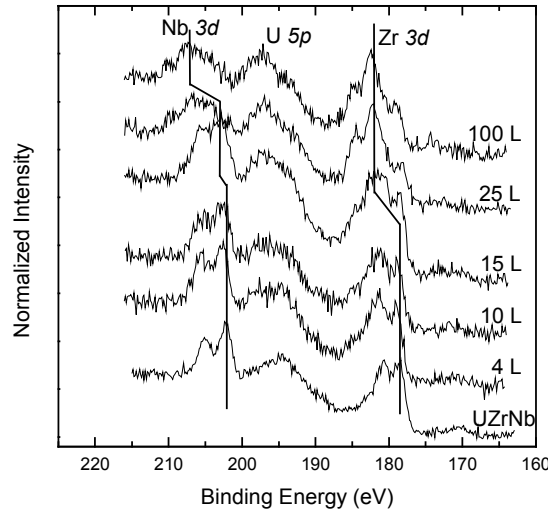


Figure 3. Detailed spectra of Nb 3d, U5 p and Zr 3d peaks before and after O₂ exposures.

However, due to the complex shape of the Nb 3d peak we cannot neglect the NbO formation during the growth of the oxide in the interface. The binding energy of the 3d_{5/2} peak is centred at 203.0 eV after 15 L of exposure, that is characteristic binding energy of NbO [5,11]. These data could be explained in two ways: it is possible the formation of Nb₂O₅, a stable oxide, followed the oxidation of Nb to NbO or the presence of this different niobium oxides in the oxide film. In a recent work [5] to U2.5Nb oxidation, it was suggested the formation of multilayers constituted of NbO and Nb₂O₅ which probable are formed due to the different O₂ activities on the surface.

The O 1s, Figure 4, analysis provides also information about the accuracy of the experiments, since it is situated around 530.0 eV. This position of the O 1s photoelectron peak is characteristic of uranium oxide formation [5]. We observe, due to the absence of the components at 533.0 eV and at 531.6 eV that H₂O and OH groups, respectively, are not present on the surface and only oxides are formed [5,8,11]. The typical component of chemisorbed oxygen could change the peak O 1s at 4 L of exposure to higher binding energies. The obtained XPS results are summarized in Table 1.

Table 1 - XPS results showing the evolution of the binding energies of the main peaks with the exposure to O₂.

Exposure	U 4f _{7/2}	U 4f _{7/2} *	U 4f _{5/2}	U 4f _{5/2} *	O 1s	Zr 3d _{5/2}	Nb 3d _{5/2}
	Binding Energy (eV)						
100 L	380.0	387.0	390.9	397.9	530.0	179.1/182.5	207.2
25 L	379.8	386.7	390.5	397.1	529.8	178.5/182.2	207.1
15 L	376.7/379.9	-	387.4/390.6	397.4	530.0	179.1	203.0
10 L	377.0/380.3	-	387.7/390.9	397.4	530.3	178.8	202.6
4 L	377.3/380.3	-	388.2/391.1	-	530.4	179.1	202.8
0	377.2	-	388.0	-	-	178.8	202.2

*satellite peak

Since the growth of oxide film is controlled by diffusion of oxygen through the oxide layer or by the surface reaction, these oxides formed on the surface of the U4Zr2Nb alloy play an important role in the growth of the oxide formed on the alloy. Probably it is due to the intrinsic nature of the oxides formed in the process. In fact, the Nb₂O₅ has different dielectric properties of the UO₂, which could disturb the charge transport inside the oxide to increase the oxide layer through the oxidation reaction. On the other hand, this mixed oxide (Nb₂O₅ and ZrO₂) formed in the metal/oxide interface could change the diffusion of the ions in formed oxide and also decrease the oxidation process by growth of a barrier to the oxygen species.

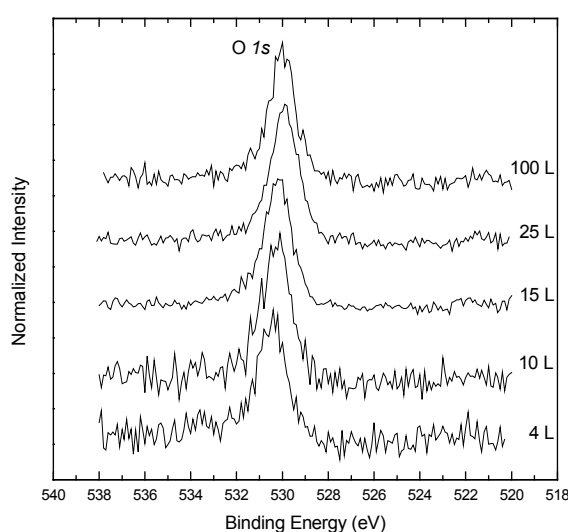


Figure 4. O 1s peaks showing no changes after exposures.

4. CONCLUSIONS

The oxide formed at low O₂ exposures on U4Zr2Nb was studied and the grown oxides are determined. Different oxides are formed on the U4Zr2Nb surface, which plays an important role in the degradation process of this alloy. These oxides (ZrO₂ and Nb₂O₅) could change the transport of ions and charge to the growth of the oxide layer formed on the U4Zr2Nb alloy due to its intrinsic defect concentration and dielectric behavior. As for the following steps, this oxidation study will be extended to other U-Zr-Nb alloys in order to finish a more systematic work.

ACKNOWLEDGMENTS

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