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XPS study of hydrogen and oxygen interactions on the surface of zirconium

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Abstract

The purpose of this study is to investigate the role of temperature and hydrogen charging conditions on hydrogen and oxygen dissolution and segregation on the surface of zirconium. X-Ray photoelectron spectroscopy was used to follow the changes as a function of temperature in the electronic properties of the surface before and after in situ or ex situ exposure to hydrogen. In situ annealing of Zr samples favors the oxygen decontamination of the surface and increases its reactivity with H. In situ (gas) or ex situ (cathodic) exposure of Zr to hydrogen at 20 °C promotes the nucleation of a Zr hydride on the surface which decomposes with increasing the temperature up to 600 °C. A segregation of oxygen on the surface is also associated with the local hydrogen enrichment.

Keywords: Hydrogen; Oxygen; Dissolution; Zirconium; X-Ray photoelectron spectroscopy; Segregation

1. Introduction

The corrosion resistance and the mechanical properties of zirconium alloys used as cladding materials in the nuclear industry are currently investigated in numerous studies [1–6]. Zirconium and Zr alloys are known to dissolve large amounts of oxygen and hydrogen [7–12] and the interactions of these species on the surface are considered to strongly control the environmental degradation of the alloy [13–15]. However little is known about the temperature dependence of these interactions and on the way they affect the electronic properties of the surface. The main purpose of this study is to investigate, using in situ X-ray photoelectron spectroscopy (XPS), the role of temperature on hydrogen and oxygen segregation on the surface of zirconium exposed to hydrogen and the consequences on the electronic properties.

2. Experimental procedure

An industrial-grade zirconium (99.7%) with 0.12% oxygen has been used in this study. The recrystallized microstructure exhibits a strong texture with small (10–15 μm) elongated grains (Fig. 1a). Detailed experimental conditions for XPS analysis are reported elsewhere [16,17]. A heating or cooling stage (-196 °C$<T<$700 °C) was used for in situ investigations of the temperature dependence of hydrogen and oxygen effects on the surface. In situ hydrogen charging was performed at room temperature in the preparation chamber under a low pressure (1 Pa) of pure hydrogen (99.999% vol.). Ex situ cathodic charging was performed in a sulfuric acid solution

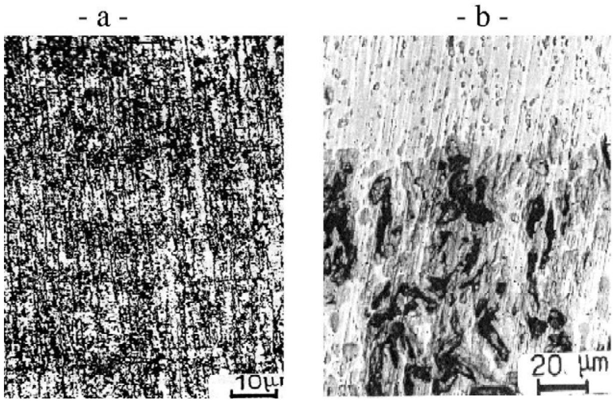

Fig. 1. Microstructures of Zr: (a) etched sample, (b) hydrogenated sample.

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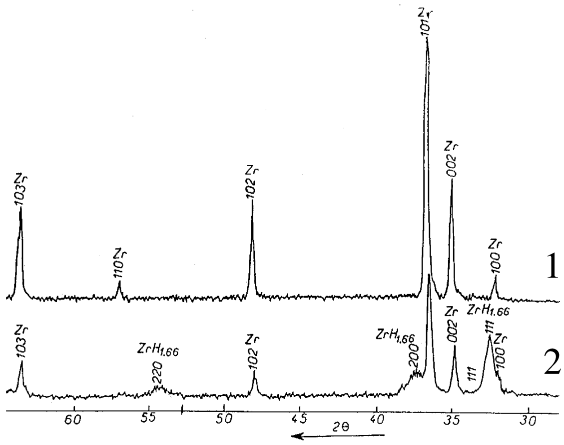

Fig. 2. X-Ray diffraction spectra of Zr (Cu Kα, 30 kV, 24 mA): (1) uncharged sample, (2) hydrogenated sample (120 min).

(0.5 M H_2SO_4+50 mg/l As_2O_3, 20 °C, 120 min, V=−1700 mV/$_{S.C.E.}$ (Saturated Calomel Electrode)) to favor the hydriding of the surface [18]. Spectra were fitted by peaks synthesis using a Gaussian/Lorentzian peak shape mixing ratio. The fitting program, enabled us to fix constant values of the area ratios for spin doublets according to the Scofield photoemission cross-sections [19].

3. Results and discussion

3.1. Hydride precipitation induced by cathodic charging

The local swelling on the surface, after cathodic charging (Fig. 1b), is presumably a consequence of the lattice expansion associated with a local hydride precipitation. The diffraction peaks, before hydrogen charging (Fig. 2—1), are in agreement with previous results [20]. After cathodic charging the spectrum exhibits extra peaks characteristics of the δ hydride (Fig. 2—2). The computed lattice parameters of the δ phase correspond to an increase of 17.6% of the hydride specific volume with respect to the Zr matrix. This value is in good agreement with those previously reported by Bai [21] and Puls [22].

3.2. XPS study of the oxygen enriched surface of zirconium

After Ar^+ sputtering to remove the natural oxide layer on the surface and before in situ annealing of the samples at different temperatures, the zirconium oxide ZrO_2 peaks are observed on the Zr3d core levels (Fig. 3a). For the specimens annealed under UHV in the analyser, the strong evolution of the spectrum with the annealing temperature illustrates a large increase of the Zr intensity and a correlative oxygen depletion of the surface (Fig. 3c). A 10-fold increase of the intensity of the Zr3d core levels is measured with increasing the temperature from 240 to 600 °C (Fig. 3a and b) and the relative Zr 'enrichment' of the surface is already significant after aging for 90 min at a temperature as low as 300 °C.

3.3. Role of cathodic charging on the electronic properties of the zirconium surface

The Zr3d core level spectrum recorded after cathodic charging at 20 °C is compared in Fig. 4a with the spectrum characteristics of clean Zr (curve 1), and of ZrO_2 (curve 2). Curve 2, together with the O1s core levels (Fig. 4b), show a strong oxygen incorporation on the hydrogenated surface. It is presumably a consequence of the reactivity of the hydrided surface with air and moisture to form oxyhydrides immediately after cathodic charging [23]. Moreover the energy shift of the O1s peak (Fig. 4b, curve 3) is in favor of the presence of OH^- bonds on the surface of the H charged specimen (cf. Section 3.5).

3.4. Role of in situ hydrogen charging

The Zr3d core levels are, respectively, located at 178.8 and 181.2 eV on the clean surface of Zr (Fig. 5a, curve 2). The in situ hydrogen charging favors a chemical shift of

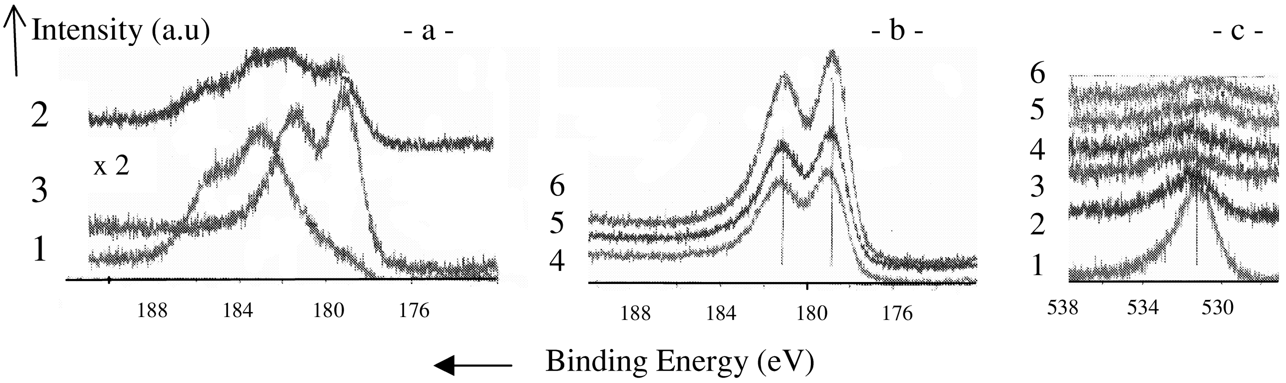

Fig. 3. XPS core level spectra of Zr in the 25–600 °C temperature range: (a) Zr3d, (b) Zr3d, (c) O1s. 1=Zr+Ar^+ 10 min (20 °C), 2=Zr+Ar^+ 10 min+90 min at 240 °C, 3=idem+90 min at 300 °C, 4=idem+90 min at 400 °C, 5=idem+90 min at 500 °C, 6=idem+90 min at 600 °C.

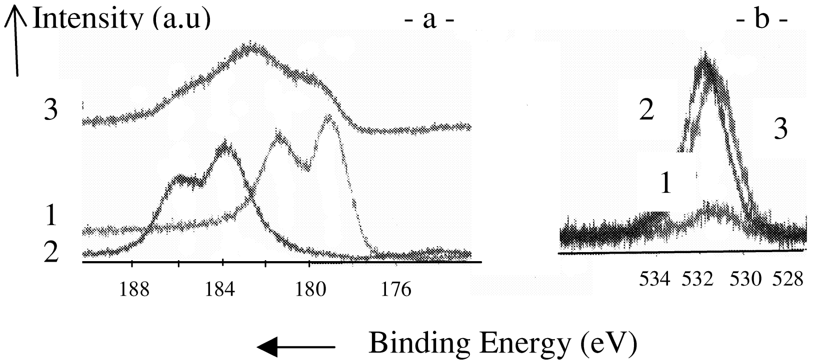

Fig. 4. Role of cathodic charging on XPS core level spectra of Zr3d (a) and O1s (b). 1=Zr, 2=ZrO_2, 3=Zr+cathodic charging, 20 °C, 120 min.

about 0.6 eV of the Zr3d core level (Fig. 5a, curve 3) which is in agreement with values already reported for the hydrogen–zirconium bonds in hydrides such as $ZrH_{1.65}$ [24] or ZrH_{imp} [25]. The additional contribution observed near 184.5 eV is the Zr3d3/2 feature of a non stoichiometric oxide (ZrO_x, $x<2$). This contribution illustrates the oxygen enrichment of the surface during in situ hydrogen charging. The Zr3d bonds of the hydride and of the oxide disappear after in situ aging for 90 min at 600 °C in UHV of the hydrogenated specimen (Fig. 5a, curve 4). This can be explained by the thermal decomposition in UHV of the superficial hydride, in agreement with thermodynamic data of the Zr–H system [26]. As expected, an opposite evolution is observed (Fig. 5b) for the intensity of the O1s spectra (state 2: intensity decreases; state 3: presence of OH^- bonds, state 4: disappearance of OH^- bonds).

3.5. Discussion

Cathodic hydrogen charging at 20 °C of Zr leads to the heterogeneous precipitation, in the superficial hydrogenated layer, of the hydride $ZrH_{1.66}$ which is stable for standard temperature and pressure (STP) conditions (Fig. 2). However the strong oxygen contamination of the hydrogenated surface (Fig. 4) is presumably a consequence of chemical interactions of the hydride with air and moisture allowing to form an hydroxide or an oxyhydride at room temperature [23].

In situ annealing of H-free Zr samples shows a rise in the intensity of Zr3d spectrum (Zr^0) with increasing the temperature while the oxygen contamination of the surface decreases (Fig. 3). This relative enrichment of the surface with Zr atoms, occurring at a temperature as low as 300 °C, is in good agreement with previous observations of the role of temperature on the dissolution of superficial oxide in Zr [10,12]. The oxygen depletion and the correlative increase in the concentration of Zr atoms on the surface is usually considered to be controlled by the diffusion of oxygen from the enriched surface toward the bulk of the Zr specimen. However, as an additional Ar^+ sputtering of the surface of the annealed specimen shows a strong raise in the O1s intensity and a sharp decrease of the Zr3d signal [27], the segregation of Zr atoms to the surface may also contribute to the temperature dependent change in the electronic properties of the surface. Additional measurements are in progress to study such a

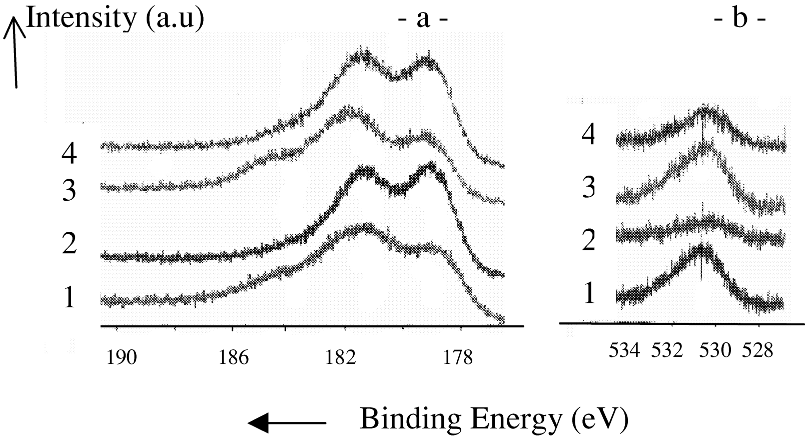

Fig. 5. Role of in situ hydrogen charging on XPS core level spectra: (a) Zr3d, (b) O1s. 1=Zr+Ar^+ 90 min, 2=Zr+Ar^+ 90 min+90 min at 600 °C, 3=idem+H_2 (40 min) at 20 °C, 4=idem+90 min at 600 °C.

mechanism of surface segregation of Zr at low temperature.

The reconstruction of the XPS spectra allows one to distinguish between the combined effects of hydrogen and oxygen on the surface of hydrogenated samples. The spectrum recorded on the oxidized surface is shown in Fig. 6a; the characteristic binding energies are 183.7 and 186 eV. The small contribution of a suboxide can be explained by electronic changes induced by Ar^+ sputtering of ZrO_2 [28]. The spectrum reconstruction for a clean Zr surface is successful with two peaks at 178.8 and 181.2 eV and two satellites representative of a suboxide (Fig. 6b). The optimal spectrum reconstruction for the cathodic hydrogen surface is obtained with four doublets (Fig. 7a). The first doublet at 179.3 eV exhibits a chemical shift of 0.5 eV with respect to the Zr3d core level of the metal; it is attributed to the hydride ZrH_2 in agreement with the literature [24,25]. The second doublet is associated with the suboxide ZrO_x with a binding energy at 180.9 eV in good agreement with the value of Wang et al. [13] and the third doublet at 182.4 eV is also attributed to a suboxide. All these suboxides may preexist in the analyzed layer but they also may be a consequence of the Ar^+ sputtering of the surface [28]. Finally, the last doublet at 183.7 eV stands for the oxide ZrO_2 (Fig. 6a), in good agreement with values of Sasaki and Baba [25]. The reconstruction of the spectrum obtained after in situ gas phase charging at 20 °C is obtained with three doublets (Fig. 7b). The first one fits with the Zr–H binding energy characteristic of ZrH_2 [24]. The second and third doublets are attributed to the same suboxides as those identified above on Fig. 7a. The good agreement obtained, for different experimental conditions, between the experimental spectrum and the reconstructed one using the same binding energies, is a good indication of the validity of the reconstruction with the selected values of binding energy. A good agreement is also obtained between the experimental O1s spectrum recorded after cathodic charging and the reconstructed one using a second peak representative of O–H bonds (Fig. 7c).

Finally it is interesting to point out the increase in the oxygen contamination of the surface associated with in situ hydrogen charging of the sample (Fig. 5). Whereas additional work is required for a precise understanding of the oxygen enrichment of the surface, this effect is not considered to be the consequence of a contamination with oxygen of the hydrogen atmosphere in the preparation chamber. It is rather associated with the hydride formation on the surface. As suggested from the results of previous studies [13] both the lattice distortion associated with H absorption and H–O attractive interactions may favor the migration toward the surface of oxygen atoms already present as impurities in the material.

4. Conclusion

The role of temperature and hydrogen charging conditions on hydrogen and oxygen dissolution and segregation on the surface of zirconium has been investigated by XPS. In situ annealing of Zr samples favors the oxygen decontamination of the surface and increases its reactivity with H. In situ (gas) or ex situ (cathodic) exposure of the Zr surface to hydrogen at 20 °C promotes the nucleation of a Zr hydride on the surface which decomposes with increasing the temperature up to 600 °C. In situ exposure to hydrogen also favors an enrichment of the surface with oxygen already present in solid solution in Zr. This oxygen contamination is ascribed to a H-induced enhancement of the segregation of oxygen atoms to the surface.

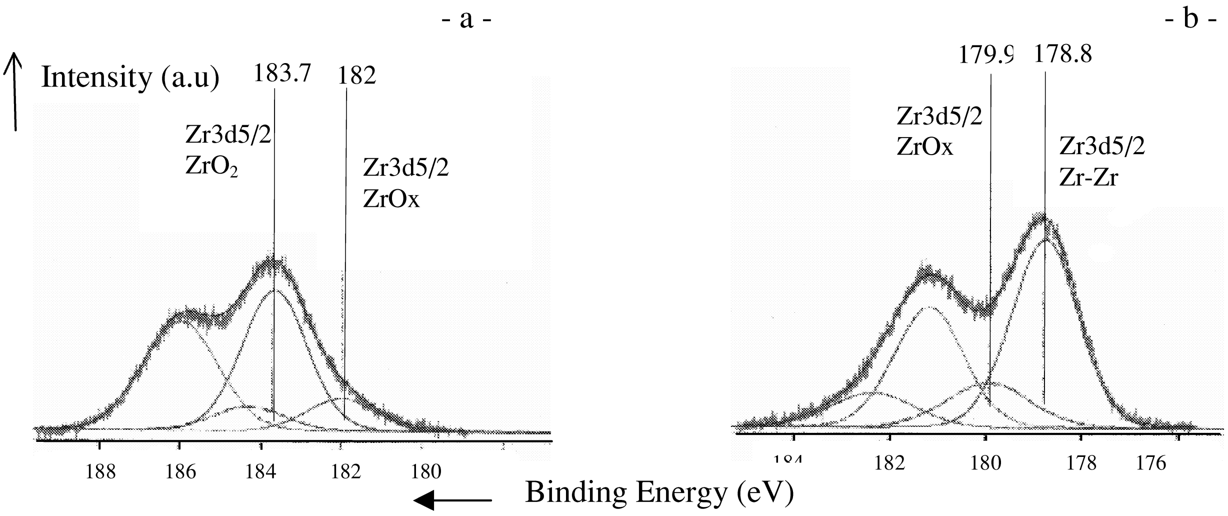

Fig. 6. Reconstruction of the XPS core level spectrum (Zr3d) on ZrO_2 (a), Zr metal (b).

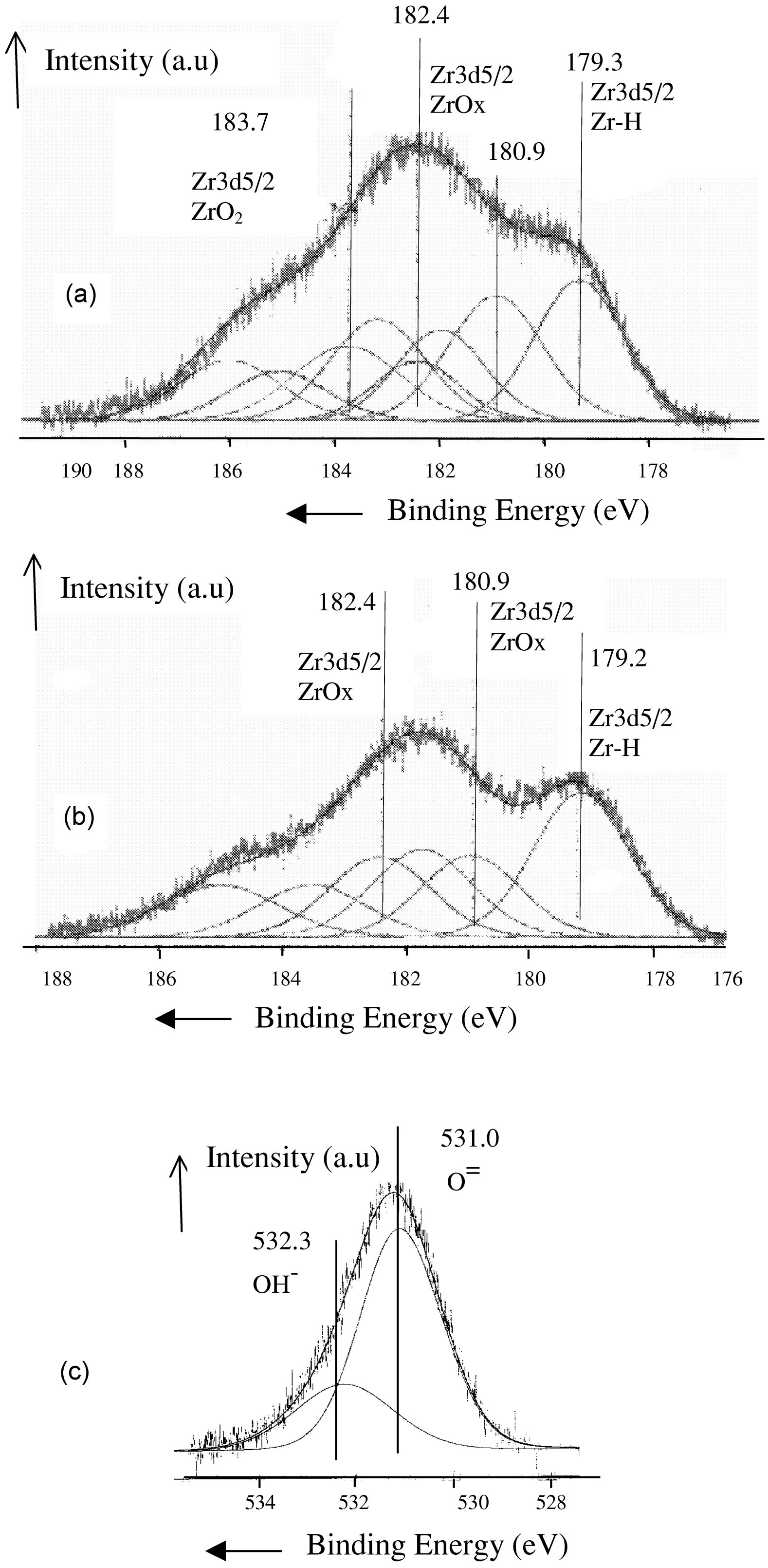

Fig. 7. (a) Reconstruction of the XPS core level spectrum (Zr3d) on Zr+H cathodic charging. (b) Reconstruction of the XPS core level spectrum (Zr3d) on Zr+in situ H gas charging. (c) Reconstruction of the XPS core level spectrum (O1s) on Zr+cathodic H charging.

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