



The interaction of Zr₂Fe surface with O₂ and H₂O at the temperature range 300–770 K

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ABSTRACT

The surface of metallic Zr₂Fe was exposed to oxygen and water vapor, in order to study the effects of these gases, being the main degradation agents in its operation as a getter for hydrogen. It was found that both gases oxidize the Zr component of the alloy surface, leaving the Fe metallic and strongly diluted. The oxidation is temperature and pressure dependent and under oxygen pressure of up to 5×10^{-6} Torr the oxide thickness increases with temperature up to ~470 K. At higher temperatures, above 570 K, the oxide film growth becomes predominated by decomposition and diffusion of oxygen into the substrate and higher oxygen pressure is needed to compensate the oxygen dissolution. It was found that for oxygen pressure of 1×10^{-5} Torr and 620 K, which is the operating temperature of the getter, the oxidation is most effective, since both the adsorption and inward diffusion are efficient. The oxide film thickness, at these conditions, is about the XPS probing depth (~5 nm). For 770 K, the dissolution and inward diffusion are very fast and the adsorption not efficient enough, leaving a dissolved and depleted oxygen layer at the surface. The initial sticking coefficients per oxygen atom, at RT, are similar for oxygen and water vapor, but the oxide thickness, obtained for H₂O, is more than twice of that for O₂, which points to a different oxidation mechanism. The presence of oxygen vacancies or incorporation of hydroxyl groups in the oxide layer may be the factors enabling further inward growth.

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1. Introduction

The Zr₂Fe alloy belongs to the non-evaporable getters (NEG) family. NEG materials have long been used in the industry for a variety of applications, which need maintaining of ultra-high-vacuum (UHV) such as high energy particle accelerators [1–3]. The most common NEG materials are metals, such as Zr, Ti, Nb, Ta, V that have a wide solubility range towards oxygen or hydrogen and alloys based on those metals. The NEG are usually easy to apply and manufacture as powder, pellets, thin layers, etc. [1–3]. Zr₂Fe was found to be effective in scavenging hydrogen down to very low concentrations and can be used, for example, to prevent the release of tritiated heavy water [4] or for fuel purification in a fusion fuel cycle [5]. It is used for a variety of applications, like gas purification from hydrogen and its isotopes [6–9], hydrogen storage [10], safeguarding of hydrogen high pressure vessels and hydrogen retrieval from several gas mixtures [6]. It has been found that this alloy can absorb hydrogen up to 46% of its volume. It can also selectively absorb hydrogen from an N–H mixture, efficiently and selectively, up to 720 K, without disintegration [11]. This absorption forms two

phases (disproportionation), ZrH₂ and ZrFe₂ [4,12]. Surface poisoning due to pre-exposure to gases like oxygen, water vapor, CO₂ and methane can reduce or even prevent hydrogen absorption [14].

The temperature effect on the surface composition of Zr₂Fe was studied by XPS [7,13,14]. It was found that heating the alloy to 470–1070 K causes a decrease of the spectral lines of oxygen contained components and an increase of the metallic ones. The atomic concentration of surface zirconium is increased to 75%, compared to the 66%, which is the nominal bulk value, on the expense of surface Fe due to surface segregation of Zr. The oxidation by oxygen was also studied by XPS and AES [15,16] at room temperature (RT), finding that sub-stoichiometric oxides are formed on the surface.

The aim of the present study is to specify and understand the degradation mechanism of the getter, by oxygen and water vapor contaminations, in the temperature range 300–770 K.

2. Experimental

The study was performed in a UHV system ($\sim 2 \times 10^{-10}$ Torr baseline pressure), which has been described in detail in previous publications (e.g. [17]), utilizing direct recoils spectrometry (DRS), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS).

The DRS is based on grazing irradiation of the surface with a pulsed beam of 3 keV Ar⁺ ions, and the time of flight measurements of the surface atoms (and ions) which are recoiled in a forward direction, following the direct collision inflicted by the impinging primary ions. The main characteristics of this technique are topmost surface sensitivity, detection of light atomic masses, including hydrogen, and being

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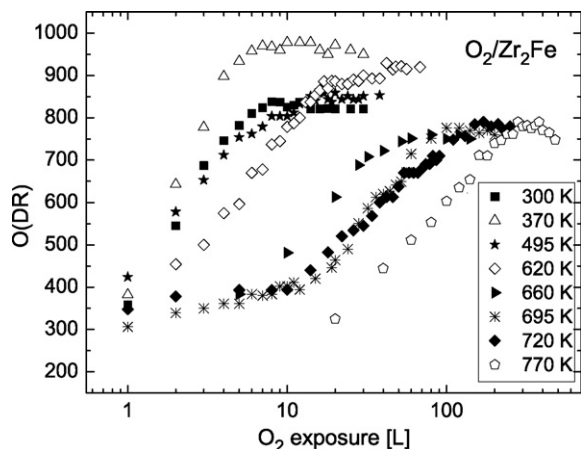


Fig. 1. O(DR) vs. exposure to oxygen (in Langmuirs) of Zr_2Fe , for various temperatures.

non-destructive, due to the low dose of impinging ions, needed for a good quality spectrum [18–20]. The combination of DRS and electron spectroscopy methods (e.g. AES, XPS) which probe to a deeper range beneath the surface, may resolve between processes occurring at the topmost atomic layer and in the subsurface region. Shadowing or non-shadowing of surface residing hydrogen atoms, make DRS an especially effective method for the differentiation between partial and full dissociation of water molecules on the surface [21,22].

The Zr_2Fe sample was gradually polished down to $1\ \mu\text{m}$ by diamond paste, cleaned in distilled water and ethanol and then attached by spot-welding to two Ta wires, which enabled heating by driving an electric current through them. The sample temperature was monitored by a Chromel–Alumel thermocouple, spot welded to the sample edge. Sputter-cleaning was performed, before each exposure experiment, by a $5\ \text{kV}\ \text{Ar}^+$ ion beam during heating the sample to $\sim 770\ \text{K}$ and then lowering the temperature (during sputtering) to the desired one, in order to achieve maximum cleanliness of the surface and to avoid possible preferential sputtering.

3 keV electrons were used for the AES measurements and a Mg ($E = 1253.6\ \text{eV}$) anode for the XPS measurements. For Zr(3d), $\lambda \sim 2\ \text{nm}$, so the XPS depth sensitivity is $\sim 5\ \text{nm}$.

3. Results

3.1. O_2/Zr_2Fe

Fig. 1 presents the O(DR) intensity vs. O_2 exposure dose (in logarithmic scale) for various temperatures, between 300 and 770 K. Two groups of adsorption curves can be observed. The first one, for the low temperature range, between 300 and 620 K, has a higher growth rate with exposure and reaches higher saturation values than the other group 660–770 K. The abrupt decrease in oxygen accumulation rate and saturation value that can be observed in the narrow range 620–660 K, will be discussed in the next section. It should also be noted that in the low temperature range, the 370 K curve, rather than that of the lowest temperature, 300 K, has the highest growth rate and saturation intensity.

Fig. 2 presents some of the RT AES spectra (Zr and Fe range) measured after steps of exposure to O_2 at pressure range of 5×10^{-7} to 5×10^{-6} Torr. The decrease of the Fe intensity and energy shift of the Zr lines, turning from metallic to oxidic, are noticeable (Zr spectrum similar to that of clean and oxidized Zr metal [23]). Peak-to-peak intensities were served for AES quantifications of oxygen and Fe. The clean and oxidized Zr components were extracted from the spectra by linear regression assuming that the measured AES zirconium spectrum is composed of a linear combination of a clean and a fully oxidized Zr signals. Fig. 3 presents the RT relative change of intensities of metallic and oxidic Zr (Zr(m) and Zr(ox), respectively), Fe and oxygen vs. oxygen exposure dose. Zr and Fe were normalized to 1 for the clean surface and oxygen to the saturation value. It is clear that Fe is depleted on the surface during oxidation (of Zr), while the sum of Zr(m) and Zr(ox) is about constant. The AES

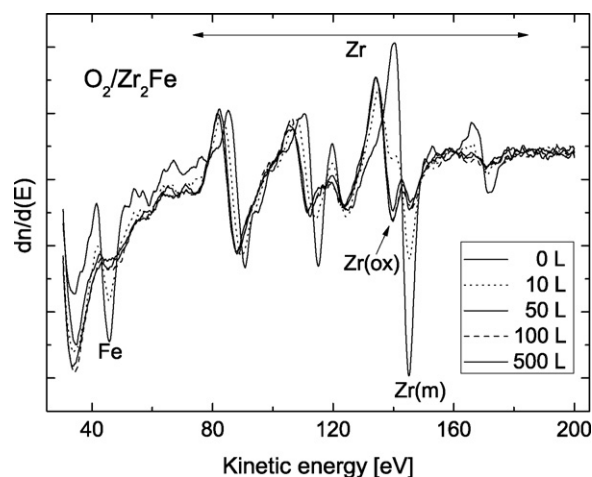


Fig. 2. Room temperature AES spectra of Zr_2Fe , clean (0L) and exposed to various doses of oxygen. The Fe line and the metal (Zr(m)) and oxide (Zr(ox)) lines of Zr, are denoted. The arrow indicates the range used for oxide thickness calculations (Fig. 13).

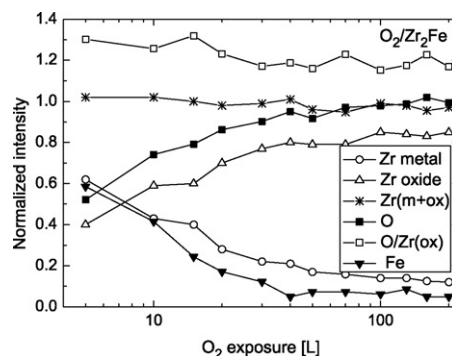


Fig. 3. Normalized (as indicated in the text) AES intensities of the Zr, Fe and O lines and also O/Zr(ox) vs. oxygen exposure dose, for RT exposures.

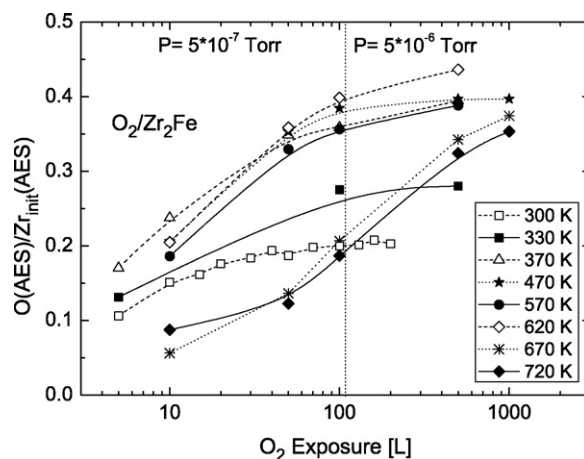


Fig. 4. O(AES) intensity (normalized to the clean Zr line) vs. exposure to oxygen, for various temperatures. The pressure of oxygen at each exposure range is indicated. The pressure of the 300 K exposure was 10^{-7} Torr.

intensity of oxygen, presented in Fig. 4 vs. exposure to oxygen, for some temperatures, presents a generally similar behavior to that of the O(DR) one (Fig. 1). The differences (that are significant) are discussed in the next section.

XPS measurements of the Zr(3d) binding energies for exposure to 1000 L O_2 at 1×10^{-5} Torr for 3 temperatures (Fig. 5), exhibit

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