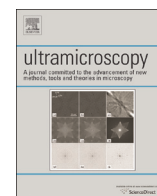




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Initial stages of oxide formation on the Zr surface at low oxygen pressure: An in situ FIM and XPS study

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ABSTRACT

An improved methodology of the Zr specimen preparation was developed which allows fabrication of stable Zr nanotips suitable for FIM and AP applications. Initial oxidation of the Zr surface was studied on a Zr nanotip by FIM and on a polycrystalline Zr foil by XPS, both at low oxygen pressure (10^{-8} – 10^{-7} mbar). The XPS data reveal that in a first, fast stage of oxidation, a Zr suboxide interlayer is formed which contains three suboxide components (Zr^{+1} , Zr^{+2} and Zr^{+3}) and is located between the Zr surface and a stoichiometric ZrO_2 overlayer that grows in a second, slow oxidation stage. The sole suboxide layer has been observed for the first time at very early states of the oxidation (oxygen exposure ≤ 4 L). The Ne⁺ FIM observations are in accord with a two stage process of Zr oxide formation.

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1. Introduction

When a “freshly-prepared” metal or semiconductor surface is exposed to an oxygen-containing atmosphere, an oxide layer is formed even at low temperatures and at low oxygen pressures. This phenomenon is of fundamental technological importance in different fields, such as catalysis, medical, biomechanical and electronic devices, fuel cell technology and photonics [1–5]. Increasing miniaturization of devices and sensors boosts the importance of the oxide-film contribution since the relative impact of the surface layer increases when downsizing metal/oxide structures [6,7].

However, the number of systems, for which a (highly desirable) atomic scale control over the oxidation processes is achieved, is still scarce and the amount of knowledge on the microscopic mechanisms of the reactions between adsorbed oxygen and solid surfaces is thus rather limited [8,9]. This is due to the chameleon-like changing character of the oxygen-surface interactions occurring on the nanoscale, which hampers a direct experimental observation. In addition, the frequent occurrence of metastable oxide structures makes difficult the use of equilibrium phase diagrams and other thermodynamic data for explanation or prediction of the atomistic mechanisms of surface oxidation [10–12].

To describe the surface oxidation of metals, a number of models has been developed, such as the Cabrera–Mott's [13] and

Fromhold's [14] models, which were continuously modified during the years [15–17]. However, these models assume a uniform oxide growth governed by the transport of species through the continuous oxide film and thus do not account for the inhomogeneities in the chemical composition, structure and morphology across the oxide layer. This stimulates extensive experimental studies both for the practical use and for the development of refined models.

Thin native oxide films formed on zirconium and zirconium-alloy surfaces are of particular interest, since they are usually dense enough to passivate the surface against the further incorporation of reactive gases into the bulk. This allows using such surfaces in high-temperature corrosive atmospheres, e.g. in nuclear reactors, but also still requires detailed knowledge on the kinetics and mechanism of growth of zirconium oxide films for understanding of passivation mechanisms [18].

Despite of the general agreement on the processes which precede oxide formation, i.e. subsurface oxygen formation, dissolution of oxygen atoms in the zirconium lattice and ordering of the O-superlattice in the subsurface layer [19,20], there is less consent on the role of suboxides in the initial Zr oxidation. Although earlier XPS studies [21–23] have already suggested that suboxides may be formed upon low oxygen exposures (0.5–2 L), the mutual proportion and even the number of the appearing suboxides are still debated. There is only agreement that the native oxide growth occurs as a two stages process where the first rapid stage of oxidation (characterized by Zr enrichment and oxygen deficiency) occurs in the region between the metal surface and the

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ZrO₂ overlayer, followed by a slower stage of ZrO₂ formation [24,25]. Moreover, in most studies the presence of suboxides is still neglected presumably due to their minor contribution to the total oxide amount. The reason is mainly the “masking” role of a much thicker ZrO₂ overlayer grown on the ultrathin suboxide interlayer, the sole suboxide layer was to our knowledge not yet observed, supposedly due to the very high rate of initial oxidation. Using the 1D atom-probe (1D-AP) technique, the “masking” problem can be circumvented and in fact, the indications were found for a composition similar to ZrO located between the ZrO₂ overlayer and the metal surface [26]. Applying the most advanced 3D-AP with laser pulsing, this finding was confirmed, however, possible miniature fractures between the oxide and the metal of the needle-shape specimen make the analysis of the transition region difficult [27]. In addition, possible grain boundaries increase the fragility of the atom-probe samples and adulterate the AP-data. Such high fragility of Zr specimens under high electric field stress hampered for a long time AP and FIM studies of Zr and Zr oxides. Thus it is highly challenging to develop a methodology for stable Zr tips fabrication for AP and FIM studies as well as to obtain reliable data on the initial oxidation of Zr.

In the present contribution we present a new method for Zr tips fabrication based on the fragmented recrystallization of a Zr wire as a result of repeated “hcp-to-bcc” and vice versa phase transitions, and the first FIM observation of Zr oxidation on a microscopic-scale. For comparison, an XPS study of the initial oxidation on polycrystalline Zr foil with emphasis on the identification of Zr suboxides was performed.

2. Experimental

The experiments were performed in two independent bakeable all-metal UHV setups with a base pressure of $\leq 10^{-9}$ mbar: (i) an FIM system which contains a tip assembly, allowing operation in a controlled temperature range of 78–900 K, a channel plate, a gas-supply system where high purity gases (Ne for FIM imaging and oxygen for Zr oxidation) can be supplied via leak-valves under mass-spectrometric control, and (ii) an XPS system with a Phoibos 100 hemispherical energy analyzer and XR 50 twin anode X-ray source (both SPECS, Germany). The XPS system is also equipped with gas supply facility and, additionally, the sample can be cleaned by argon ion sputtering. More details of the experimental setups can be found elsewhere ([28] for XPS and [29] for FIM/FEM).

As already mentioned, an improved methodology for the Zr tip preparation was elaborated in present work, based on the supposition that the low stability limit of Zr nanotips in previous studies originates from the small size of the crystallites. To increase the size of crystallites, a Zr wire (0.127 mm diameter, Alfa Aesar, Fig. 1a) was preliminarily annealed in UHV under mechanical tension. After conventional annealing at 973 K for several hours, as used in most other studies for Zr sample preparation, the surface became clearly smoother. During the further annealing at 1173 K for 4 h, fragments of small monocrystals (~ 0.3 mm, Fig. 1b) were formed as a result of the “hcp-to-bcc” phase transition at 1143 K accompanying the recrystallization. This was clearly visible as a drop in the (continuously monitored) electrical resistance despite of the increasing temperature. The reverse “bcc-to-hcp” transition was performed via slowly cooling down the annealed Zr wire, in order to prevent the distortions and corrugations resulting from the martensitic-like transition. At cooling rates lower than 25 K/min we succeeded in conserving the fragmented structure and smooth surface down to room temperature.

The Zr nanotips were then prepared from the mono-crystalline fragments of such an annealed and recrystallized Zr wire via two

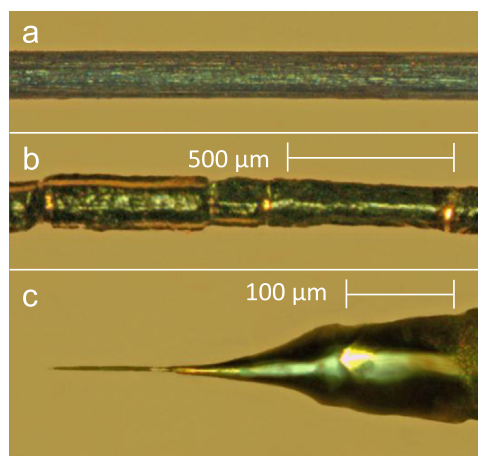


Fig. 1. Fabrication of a stable Zr nanotip. a) primary material: commercial Zr wire, 0.127 mm diameter, Alfa Aesar; b) the same wire after annealing at 973 K for several hours and after the formation of small monocrystals at 1173 K; c) a Zr nanotip fabricated by electro polishing from the monocrystal visible at right side of the Fig. 1b.

stage electro polishing. In the first stage we used a DC “dip etching” at 15 V/150 mA with a H₂O/HClO₄/CH₃COOH mixture of the ratio 10/15/75. In the final stage the DC microscope-zone-polishing at 0.1–5 V DC by H₂O/HClO₄/2-butoxy-ethanol of the ratio 1/1/98 was used.

To compare the nm- and μm- scaled samples, a polycrystalline Zr foil was used for the XPS measurements (10 × 10 mm², thickness 0.2 mm, MaTeck, 99.8% purity). The foil sample was thoroughly polished before to be mounted on a standard SPECS/Omicron sample holder equipped with the thermocouple contacts.

The temperature of the specimen was measured by a NiCr/Ni thermocouple spot-welded to the front side of the foil. To minimize the contamination by segregating Fe (usual contamination in Zr foils) several standard UHV cleaning procedures, namely Ar⁺ ion sputtering (Ar pressure 10⁻⁵ mbar, E_{kin} = 1.7 keV), following by annealing at 1173 K was performed under XPS control. At the last stage, the foil sample was subjected to exactly the same thermal treatment as Zr wire to ensure the same surface condition as on the Zr tip.

3. Results and discussion

3.1. FIM observations

Because of the high fragility of Zr specimens, FIM imaging of the Zr surface with Ne⁺ ions (at ~ 35 V/nm) is a difficult task, in addition, the evaporation field of Zr at e.g. 77 K ranges below of the BIF (best image field) value for Ne. The only published FIM image of Zr with atomic resolution is that by Carroll and Melmed at 30 K [30], i.e. far below the liquid nitrogen temperature. Nevertheless, using the new preparation technique, a sufficient stability of Zr specimens was achieved for the Ne⁺ FIM imaging at 77 K. Fig. 2a shows a Ne⁺ FIM image obtained at applied field of 33 V/nm during continuous field evaporation. A set of the video-frames (Fig. 2b), monitoring the field evaporation of the (112) facet and Fig. 2c showing the dependence of the Zr evaporation rate at 77 K on the applied electric field, illustrate the stability of the Zr sample in a wide range of applied electric field. Although at the instant of field evaporation, as was shown by earlier DFT calculations [31], the positions of the surface (imaged) atoms can slightly change along the applied field direction (i.e. perpendicular to the surface), the acquired FIM images are still 2D projections with unchanged lateral distances, i.e. they reflect the correct

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