Interactions Of Oxygen, Hydrogen And Water With Zr(0001) And Zr(1010)

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INTERACTIONS OF OXYGEN, HYDROGEN AND WATER
WITH Zr(0001) AND Zr(10\bar{1}0)

by

Bing Li

Department of Chemistry

Submitted in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Ontario
April 1996

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ABSTRACT

The interaction of oxygen, hydrogen and water with Zr(0001) and Zr(10\bar{1}0) has been studied by surface science techniques. A hopping model of the diffusion of adsorbed species from a surface into the bulk has been formulated and solved mathematically. Applying this model to our AES results on oxygen dissolution, we obtained the Arrhenius expressions for diffusion as: \(0.115\exp(-44.45\text{ kcal/RT})\) cm\(^2\) s\(^{-1}\) along <0001> and \(1.07\exp(-46.18\text{ kcal/RT})\) cm\(^2\) s\(^{-1}\) along <10\bar{1}0>.

Oxide dissolution was studied by measuring the change of the oxide thickness at a series of temperatures for a constant initial coverage prepared at a fixed and low temperature. The rate-controlling step in oxide dissolution is O diffusion into bulk Zr.

The bond between H (D) and Zr on a Zr surface is energetically similar to those in zirconium hydride. There are two types of adsorption site for H adsorption, one above the surface and another in the subsurface region. Hydrogen has a very strong tendency to segregate to a Zr surface. Measured by the kinetics of the surface segregation, the diffusion coefficients of hydrogen can be determined as \(3.40 \times 10^4\exp(-9565/RT)\) cm\(^2\) s\(^{-1}\) along <0001>, and \(1.73 \times 10^3\exp(-8887/RT)\) cm\(^2\) s\(^{-1}\) along <10\bar{1}0>.

The adsorption of D\(_2\)O at 80 K can be divided into three stages: a chemisorbed layer (coverages between 0 and \(\sim 0.25\) ML), second adsorbed layer, (up to a total coverage of \(\sim 0.65\) ML) and an ice layer. The D\(_2\)O in the chemisorbed layer is probably all dissociated into OD\(_{ad}\) and D\(_{ad}\), or O\(_{ad}\) and D\(_{ad}\). The second adsorbed layer is molecular water and begins to form before the chemisorbed layer is fully saturated. Molecular water
can desorb from this layer at 173 K. The ice layer begins to form before the second
adsorbed layer is fully covered, and desorbs with zero order kinetics at 163 K.
ACKNOWLEDGEMENTS

I would like to express my appreciation to Peter Norton, my supervisor, for his advice, encouragement and assistance throughout this work. To Alan Allnatt, my co-supervisor, for his patience and guidance in developing the diffusion theory. To Chunsi Zhang, for his supervision, assistance and friendship over past eight years. To Keith Griffiths, for his supervision everywhere, especially in the water reaction project. To Jan O'Dacre and Lawrence Green for their valuable technical assistance.

Finally, I gratefully acknowledge the Scholarship in Cooperative Materials Research for Ph.D from Ontario Centre for Materials Research.
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<td>AES</td>
<td>Auger Electron Spectroscopy</td>
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<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
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<tr>
<td>FTIR-RAS</td>
<td>Fourier Transform Infrared-Reflection Absorption Spectroscopy</td>
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<tr>
<td>H</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>IMFP</td>
<td>inelastic mean free path</td>
</tr>
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<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
</tr>
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<td>NRA</td>
<td>Nuclear Reaction Analysis</td>
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<td>O</td>
<td>Oxygen</td>
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<td>SIMS</td>
<td>Secondary Mass Spectroscopy</td>
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<td>SSIMS</td>
<td>Static Secondary Mass Spectroscopy</td>
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<td>TDS</td>
<td>Thermal Desorption Spectroscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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<td>Zr</td>
<td>Zirconium</td>
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CHAPTER 1 INTRODUCTION

Because of its low neutron absorption cross section, zirconium alloys are widely used in the nuclear industry. In the CANDU (Canadian Deuterium Uranium) nuclear reactor, zirconium alloys serve as the materials for pressure tubes, calandria tubes and fuel bundle sheaths [1, 2]. Figure 1.1 is a schematic diagram of a fuel channel for a CANDU reactor with pressurized heavy water coolant. The CANDU core typically contains about 400 or more such fuel channels which are comprised of a central pressure tube surrounded by a calandria tube, which separates the pressure tube from the heavy water moderator. The fuel is contained inside the pressure tube. Heavy water flows over the fuel, and is heated from about 250 °C at the fuel channel inlet to about 350 °C at the outlet in the approximately 0.7 seconds it takes the water to transit the core. Irradiation, principally gamma rays, electrons and alphas and fission products, initiates water decomposition and produces oxidizing species in the water in the core. Between the pressure tube and the calandria tube is the annulus gas, CO₂. Irradiation also changes the chemistry of the annulus gas, particularly in the presence of various common impurities, such as hydrocarbons and hydrogen isotopes. The pressure tube is fabricated from a zirconium alloy, Zr-2.5%Nb, in order to optimize the reactor's neutron economy whilst retaining adequate corrosion resistance and strength.

The ingress of deuterium and the formation of deuterides are the main reason for the pressure tube rupture in Pickering Nuclear Generating Station in 1983. It is assumed that some of the hydrogen (deuterium) liberated by the corrosion reaction diffuses and is
Figure 1.1 Schematic diagram of a fuel channel for a CANDU reactor with pressurized water coolant
absorbed by the zirconium alloy. Although zirconium has a strong affinity for hydrogen isotopes and for oxygen, the solubility of hydrogen in zirconium is very low. At room temperature the solubility limit is less than 1 ppm, and at 300 °C, is approximately 100 ppm. Thus, at room temperature any hydrogen in excess of 1 ppm is present as solid hydrides. Zirconium hydrides are very brittle, and tend to form at areas of high local stress, hence causing fracture of the hydrides. The hydride, which appears as platelets oriented perpendicular to applied or residual stress gradients, can cause failure of the host zirconium.

The reactor pressure tubes that are made from such alloys are coated with an oxide (24 hours of 400 °C steam) before introduction into the reactor. This oxide layer is expected to serve as a barrier to prevent the possible ingress of the hydrogen from the environment. However, the zirconium oxide begins to dissociate and oxygen begins to dissolve into the bulk metal at the reactor operating temperature. Some questions naturally arise about the lifetime, and its effectiveness as a barrier for hydrogen ingress, of the oxide coating.

Large efforts have been made in studying the ingress of hydrogen, break down of the zirconium oxide layers, the behavior of the oxide-metal interface and the influence of impurities in alloys, etc. However, little is known about the microscopic mechanisms that underlie the corrosion process [1], which is schematically illustrated in Figure 1.2.

The work presented in this thesis is focussed on the interaction of oxygen, hydrogen and water with the zirconium surface. Various surface techniques were employed in this study. These techniques, which will be briefly introduced in the chapter 2,
Figure 1.2  Schematic illustration of the process of hydrogen ingress
include Auger electron spectroscopy (AES [3]), low energy electron diffraction (LEED), work function (Δφ), secondary ion mass spectroscopy (SIMS), nuclear reaction analysis (NRA), Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS), and thermal desorption spectroscopy (TDS). Chapter 3 presents a new theory to model the diffusion process in the near surface region. Based on this model, the diffusion coefficients of the oxygen at a relative low temperature can be determined in a fairly simple method by using the surface science techniques. This parameter is important in studying the stability of the oxide barrier outside the zirconium pressure tube. Chapter 4 shows the process of hydrogen adsorption and segregation at the zirconium surface, which is helpful in understanding the kinetics and chemistry of the formation of the hydrides. Chapter 5 is the study on the corrosion reaction between zirconium metal and the heavy water coolant. The major results are summarized in chapter 6.

The reprints, or preprints, of the published papers are appended to provide the detailed and extended studies on these subjects. Appendices I and II give more details on the diffusion theory and the oxygen diffusion discussed in chapter 3. Appendices III and IV show the extended discussion on chapter 4. Appendix V gives more details on the study presented in chapter 5.
References


[3] All of the abbreviations throughout his thesis are listed in page xiv.
CHAPTER 2 METHODS

2.1 Sample Preparation

The Zr(0001) and Zr(1010) samples were cut from a 99.99% pure zirconium single crystal rod of 5 mm diameter provided by Chalk River Nuclear Laboratories of Atomic Energy of Canada Ltd. They were aligned by X-ray diffraction to within ± 0.5° of the chosen planes and mechanically polished with increasingly fine grades of diamond paste. A chemical etch with a 50:45:5 HNO₃/H₂O/HF solution was made between the mechanical polishings.

The sample was supported by spot welding to two platinum wires which were mounted between nickel-terminated copper posts connected to the sample manipulator. A K-type thermocouple was spot welded to the top edge of the sample. The manipulator could be filled with liquid nitrogen allowing sample temperatures as low as 90 K to be realized. The sample was heated by directly passing current through the support wires. The sample temperature could be raised at a rate of 70 K/sec and cooled at 50 K/sec. The temperature overshoot during the heating was controlled within 2 - 3 K by a programmed temperature controller.

The sample cleaning procedure involved ion bombardment under a low base pressure ( < 1 x 10⁻¹⁰ Torr), a low CO pressure ( < 1 x 10⁻¹¹ Torr) and clean argon sputtering gas. The sample, after being mounted in the UHV chamber, was first bombarded by 3 kV Ar⁺ ions at a current density of about 3 μA cm⁻² for 1 hour to remove the original oxide layer and other contaminants (C, Cl, and F). During continuous
sputtering, it was then heated to 1023 K for 30 min (to segregate the impurities of S and P to the surface region), then cooled to 450 K for 30 min to remove the segregated H, and finally cooled to room temperature for another 30 - 45 min sputtering. This process produced an AES clean surface (C 1 - 2 at % and Cl, F, and O below the AES noise level, i.e., < 0.5 at %). A brief anneal at 923 K produced a sharp (1 x 2) LEED pattern for the (0001) surface and (1 x 4) LEED pattern for the (1010) surface.

The experiments were mainly performed in two stainless steel ultrahigh vacuum (UHV) chambers. The LEED, Δϕ, SIMS, TDS, AES and NRA were carried out in a double level UHV chamber. The manifold connected to the chamber is equipped with several leak valves which allows the sample to be exposed to known pressures of various gases. The chamber is pumped by liquid nitrogen trapped diffusion and Ti sublimation pumps which allows base pressures of < 5 x 10⁻¹¹ Torr to be achieved. The second chamber equipped for IRAS, Δϕ and TDS is pumped by a turbo-molecular pump backed by a diffusion pump and operates in the 10⁻¹⁶ Torr range. H₂O or D₂O can be dosed onto the sample by a molecular beam nozzle or shuttered capillary array doser. The molecular beam was produced by a source (glass capillary, 1.5 cm long, 0.05-cm diameter, source D₂O pressure ~3.5 kPa) and a number of collimated, differentially pumped apertures. Liquid nitrogen cooled tubes concentric with the beam removed scattered water. The final nozzle was a tube, 2 cm long, 0.2 cm in diameter, which protruded into the experimental chamber. With the sample placed ~ 1 cm from the beam nozzle, thermal desorption measurements of water condensed on the cooled sample indicated a negligible divergence of the water beam which is estimated to have a diameter of 0.2 cm. A beam stop inserted
before the final nozzle effectively cuts off the flow of water in less than 1 sec. The water beam delivered a very reproducible continuous flux when the water source assembly (water container and source capillary) was kept at a constant temperature of 30 °C by using a thermostatically controlled enclosure. The water flux was measured to be $9.72 \times 10^{12}$ molecules cm$^{-2}$ s$^{-1}$ or equivalent to a pressure of $2 \times 10^{-4}$ Torr.

2.2 Auger electron spectroscopy (AES)

When a core electron in an atom is removed by some process, the atom may relax in a number of ways. As an electron from an outer shell makes the transition to fill the hole, energy may be released as a photon (X-ray emission) or it may be transferred to another electron (in the same shell or higher) which is emitted from the atoms with some kinetic energy. The emitted electron is called an Auger electron. This process is illustrated in Figure 2.1 for the ABC Auger transition. The kinetic energy of this transition $E(ABC)$ may be given by [1]

$$E(ABC) = E_A - E_B - E_C - U - \phi_3$$

(2.1)

$$U = H - P$$

(2.2)

where $E_A$, $E_B$ and $E_C$ are the one-electron binding energies of the A, B and C level, respectively. $U$ is the repulsive hole-hole interaction energy which decreases the kinetic energy of the Auger electron. $H$ is the hole-hole interaction energy in the free atom and may have a correlation with the second ionization energy of the zirconium atom. $P$ is the effect of relaxation by the solid environment and is expected to reduce the interaction energy $U$. $\phi_3$ is the work function of the spectrometer.
Figure 2.1  Schematic diagram of an ABC Auger transition
The Auger electron current, $I_A$, is a function of the current of primary electron beam $I_p$, ionization cross section $\sigma_A$ at energy level A, the probability of Auger transition $P_{ABC}$, the surface roughness factor $R$, the primary electron backscatter factor $r$, and the atomic density $N$. The Auger electron from the underlayer may also travel to the surface without loss of energy. The average distance for electron travel without loss of energy is called the mean free path of the electron, denoted by $\lambda$. So the Auger electron yield is the sum of the yield from the surface as well as from the bulk [2].

$$I_A = \int_0^\infty I_p R\sigma_A P_{ABC} T N r e^{-z/\lambda \cos \theta} dz = I_p R\sigma_A P_{ABC} T N r \lambda \cos \theta$$ (2.3)

where $\theta$ is the electron collection angle measured with respect to the surface normal (42°), $e^{-z/\lambda \cos \theta}$ is the attenuation factor for the Auger signal to travel from a distance $z$ under the surface to the surface, and $T$ is the analyzer transmission factor. If the incident primary beam is at an angle $\alpha$ to the normal of the surface, then

$$I_A = (I_p \cos \alpha) R\sigma_A P_{ABC} T N r \lambda \cos \theta$$ (2.3a)

The Auger spectrometer employed was a Perkin-Elmer single pass cylindrical mirror analyzer (CMA). A small electron gun mounted along the axis of the cylinder provides the excitation beam which can be rastered across the surface by deflection plates built into the front of the gun. Electrons that are emitted by the sample are collected at an angle of 42° with respect to the surface normal. The energy analysis is done by varying the DC voltage on the outermost of two concentric cylinders which directs electrons of
the proper energy to strike the electron multiplier situated at the end of the spectrometer. Since the Auger signal is superimposed upon a large continuous background of secondary electrons (produced by the excitation beam), the signal is usually differentiated to increase the sensitivity. This is accomplished by superimposing a small AC voltage (a few volts) of kHz frequency on top of the outer cylinder voltage. A lock-in amplifier detects signal changes which can be output to a plotter or recorded by computer. The schematic illustration of this process is shown in Figure 2.2.

The quantitation of the AES data is accomplished using sensitivity factors, which can be formulated as [3]

\[ c_i = \frac{I_i/S_i}{\sum_j I_j/S_j} \]  

(2.4)

where \( c_i \) is the composition, \( S_i \) is the sensitivity factor of element \( i \) from a certain Auger transition which can be looked up in the manual [3]. In some cases, the distribution of the elements along the depth is not uniform. The mean free path of the Auger electrons has to be taken into account.

2.3 Low energy electron diffraction (LEED)

Electrons with low kinetic energies (30 - 300 eV) have de Broglie wavelengths (2.2 - 0.7 Å) that are on the order of the interatomic spacing in solids. Single crystal surfaces, because of their periodic nature, yield diffraction patterns when irradiated by a monoenergetic beam of low energy electrons. Hence, the technique of low energy electron
Figure 2.2  Schematic illustration of the Auger electron detection process
diffraction can be used to study the surface structure of single crystals and the ordered structures which are sometimes produced when atoms are adsorbed onto such surfaces [1, 4].

Diffraction from a two dimensional lattice follows the equation

\[
\frac{(s - s_o)}{\lambda} = H_{hk} + N \tag{2.5}
\]

where \(s_o\) and \(s\) are the incident and diffracted vectors respectively, \(\lambda\) is the length of the electronic wave, \(H_{hk} = h a^* + k b^*\) is the vector of the point \((h, k)\) at its reciprocal lattice plane \(N\). Generally, the magnitude of the unit vector of the reciprocal lattice is inversely proportional to that of the real lattice. As the surface is a two dimensional plane, the unit axis in the direction perpendicular to the surface is infinity. Therefore the unit vector of the corresponding axis in the reciprocal lattice has a value of zero, and the reciprocal pattern of the surface is a group of rods extended in the direction perpendicular to the surface.

The LEED pattern is actually the projection of the intercepts of the reciprocal rods to a sphere with a radius of \(1/\lambda\) (Ewald sphere). Figure 2.3 shows a schematic explanation of this process for the case in which the incident vector has an angle to the surface normal.

The adsorption of gases on single crystal surfaces may form an ordered structure [5]. Such ordering will give rise to diffraction spots in addition to those of the substrate. The diffraction pattern of the adsorbed particles has a geometric relationship to the diffraction pattern of the substrate, because the ordering of the adsorbed particles has some relation to the ordering of the substrate. Figure 2.4 shows the relationship of the real space and LEED patterns for different adsorption conditions.
Figure 2.3  Determination of diffraction direction by two dimensional reciprocal lattice and the Ewald sphere
Figure 2.4 Various real space adsorbate structures and the corresponding LEED patterns. Filled circles: substrate atoms and LEED spots. Hollow circles: adsorbate atoms and LEED spots. Adapted from reference [1].
2.4 Work Function ($\Delta \phi$)

The work function ($\phi$) of a crystal surface is defined as the energy needed to remove an electron from the Fermi level to a point just outside the crystal

$$\phi = D - \mu$$  \hspace{1cm} (2.6)

where $D$ is the surface dipole and $\mu$ is the chemical potential (the difference in the energy of the crystal with $N$ electrons and $N - 1$ electrons). The surface dipole can be affected by adsorbates but $\mu$ is not, since it is a bulk property. For surface studies, the absolute value of the work function is usually not measured, but rather changes in the work function ($\Delta \phi$) which occur upon adsorption of atoms or molecules.

The best methods can measure $\Delta \phi$ to $\pm 1$ mV. Assuming that a monolayer of adsorbate causes a change in $\Delta \phi$ of 1 V, the lower limit of detection is a few thousandths of a monolayer. The induced change in $\Delta \phi$ will vary according to the system being studied and hence its sensitivity as well. The direction of change of $\Delta \phi$ with coverage can sometimes give information about the location of an adsorbate. Figure 2.5 shows the changes expected when oxygen atoms adsorb on a metal surface. Oxygen is more electronegative than the metal and will attract electron density to itself. If oxygen adsorbs in an on-top site, the induced surface dipole is oriented so that the negative end is outward and results in an increase in $\Delta \phi$. For oxygen that adsorbs and moves to sites just below the surface of the metal, the dipole is reversed and $\Delta \phi$ decreases. Oxygen located in the first plane of surface atoms will cause little or no change in $\Delta \phi$. Another possibility is that the oxygen may move below the surface to deeper sites. In this case, the conduction electrons of the metal screen the induced charge and $\Delta \phi$ shows little or no change. The
Figure 2.5  Change in $\Delta \phi$ expected for an oxygen atom interacting with a metal near the metal surface. Circle indicates an oxygen atom; + and - signs indicate the sign of induced charges.

Figure 2.6  Schematic diagram of $\Delta \phi$ measurement using a Kelvin probe
screening is more effective the higher the electron density of the metal but typical screening lengths are on the order of a few Å. Hence, $\Delta \phi$ measurements are very surface specific.

The measurement of $\Delta \phi$ was carried out using a Kelvin probe which could achieve RMS noise levels of 1 mV at response speeds of ~ 100 ms. The most important part of the probe is a stainless steel reed with a molybdenum tip. It forms one half of a capacitor, and the zirconium crystal forms the other half. This reed is made to vibrate at a frequency of 700 - 800 Hz to form a vibrating capacitor. The current from this vibrating capacitor is

$$I = \Delta C \left( \phi_s - \phi_r \right) \omega \cos(\omega t)$$

(2.7)

Where $\Delta C$ is the change of capacitance, $\omega$ is the frequency of the vibrating reed and $\phi_s - \phi_r = \Delta \phi$ is the contact potential difference and $\phi_s$ and $\phi_r$ are work functions of the surface and the reference molybdenum tip respectively. The work function of the molybdenum tip does not change on adsorption. This is evidenced by the same $\Delta \phi$ in a repeated adsorption after cleaning the crystal. When a voltage $V_s$ is applied to cancel out this $\Delta \phi$, the current $I$ defined in equation 2.7 goes to zero. Any change in $\phi_s$ of the sample will result in a change in surface work function $\Delta \phi$ or change in $V_s$. Since $\phi_r$ is a constant, the applied voltage $V_s$ is a measure of the surface work function $\phi_s$. The vibration from the reed is detected by a piezo crystal which feeds a signal into a phase-locked loop. This loop controls the vibration of the reed at a fixed frequency. A schematic of the experimental set-up is shown in Figure 2.6.
2.5 Secondary ion mass spectroscopy (SIMS)

When ions of a few eV to tens of keV energy impact a solid surface, some of the dissipated energy results in the sputtering of material from the surface. Most of the outgoing atomic or molecular species are neutral but a small percentage are ionized (~1%). These secondary ions (usually sputtered by the primary ion beam) can be mass analyzed and provide information about the composition of the surface being bombarded. The removal of material puts SIMS in the class of destructive techniques, but it can be used in a way so as to minimize the damage caused. The two modes of use are generally spoken of as dynamic SIMS (DSIMS) and static SIMS (SSIMS) [6]. DSIMS involves high primary beam current densities which can be up to some mA/cm², under which bombardment the surface is continually eroded away. Depth profiles of several μm s can be performed in short times providing in-depth analysis of solid materials. SSIMS is realized when the primary beam current density is lowered to such an extent that the lifetime of monolayer of material on the surface of the solid is extended to several hours. Current densities on the order of 10⁹ A/cm² are needed for static SIMS. Although damage still occurs, this magnitude of current density drastically reduces the probability that the same area of the surface will be struck more than once by an ion.

The sputtering process has been studied extensively [7]. Early theories tried to link sputtering to thermal effects and evaporation but were not successful. The theory that best describes the quantitative aspects of sputtering is the collision cascade model of Sigmund [8]. The theory describes the loss of energy of the primary particle to a series of collision
cascades in which energy is transferred to target atoms. Target atoms can be moved from their positions and dissipate their energy to neighboring atoms in the solid. Sputtering occurs when enough energy is transferred to surface atoms to overcome the surface binding energy. Angular collisions contribute to the redirection of some of the initial energy back toward the surface. The sputtering material originates from depths no greater than 5 to 8 Å which makes SIMS a very surface sensitive technique.

Ions can be detected in a number of different ways. The simplest is a quadrupole mass spectrometer. They are relatively inexpensive and easy to use but do not provide very high mass resolution and the transmission is quite low (~ 10^4). Magnetic and electric sector SIMS instruments provide energy filtering and high mass resolution with somewhat higher resolution.

2.6 Nuclear reaction Analysis (NRA)

The application of nuclear reactions to surface studies has greatly aided in the quantitative analysis of adsorbates on surfaces. In general, a nuclear reaction has the form

\[ X + a \rightarrow Y + b + Q \]  

(2.8)

where \( X \) and \( Y \) are heavy nuclei, \( a \) and \( b \) are light nuclei and \( Q \) is the energy balance usually given in MeV [1]. This reaction can also be abbreviated to \( X(a, b)Y \).

The reactions employed in our work to determine the absolute coverage of oxygen and hydrogen are \(^{16}\text{O}(p, \alpha)^{14}\text{N} \) and \(^2\text{H}(^3\text{He}, p)^4\text{He} \), respectively. The primary ion used in \(^{16}\text{O}(p, \alpha)^{14}\text{N} \) reaction is a 750 keV proton while those used in \(^2\text{H}(^3\text{He}, p)^4\text{He} \) reaction are 630 keV \(^3\text{He} \) ions. The energy for the primary ion beam is selected so that the cross
section of the reaction between the ion and oxygen or hydrogen is maximum, while the cross section of the reaction between the ion and zirconium is very small. Thus NRA is very sensitive to the amount of hydrogen or oxygen at the surface.

The probability of an incident particle of sufficient energy reacting with a target nucleus is related to the geometrical cross section of the target nucleus. Nuclear reaction cross sections ($\sigma$) are dependent on incident particle energy and sometimes contain resonances where the cross section exhibits a peak with a large value in a small energy range. The yield of emitted particles, $Y$, is given by

$$Y = N \sigma(E, \theta) \Omega Q$$  \hspace{1cm} (2.9)

where $N$ is the areal density of emitting atoms (atoms/cm$^2$), $\sigma(E, \theta)$ is the cross section which depends on the energy of the incident particles ($E$) and the measuring angle ($\theta$), $\Omega$ is the detection solid angle and $Q$ is the number of incident particles. If the material is all at the surface, $N$ becomes the surface coverage. To convert the emitted yield to absolute coverage, we use a standard containing known elemental densities. When the sample is placed in the same geometry as the standard, the detection solid angle terms cancel. The only requirement is to know the area density of the standard and to take into account the number of incident particles and the relative cross sections. The standard used in our experiment is a Ta$_2^{16}$O$_7$/Ta$_2^{16}$O$_5$ oxide layer grown on Ta metal. The nuclear reaction employed in measuring the standard is $^{16}$O(d, p)$^{17}$O. The absolute coverage of the sample can be calculated by comparing the emitting yields to the standard and the known ratios of the cross sections [11] of the nuclear reactions for $^{16}$O, $^{18}$O and $^{3}$He.
2.7 Fourier Transform Infrared Reflection Absorption Spectroscopy (FT-IRRAS)

The frequencies of vibrational modes in molecules are of the order of $10^{13}$ s⁻¹, which falls in the range of frequencies of infrared radiation. If the bond has a non-zero dipole moment, infrared radiation can be absorbed and a vibrational spectrum of the molecule can be obtained. For a simple diatomic molecule with mass $m_1$ and $m_2$, the natural vibrational frequency of a bond is expressed as

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

(2.10)

where $k$ is the force constant and reduced mass $\mu = m_1m_2 / (m_1 + m_2)$.

FT-IRRAS is a technique which permits vibrational spectra of adsorbed molecules on metal surfaces to be obtained. In the reflection experiment, only light polarized with the electric field parallel (p light) to the plane of reflection excites the infrared active modes of the adsorbed molecules on reflection. At all angles of incidence, the electric field perpendicular to the plane of reflection, $E_p$, undergoes a phase change of 180 degrees and the resulting standing wave has a small field. For the p polarization, the resultant amplitude of the incident and reflected electric fields at the surface can be resolved into two components shown in the equations below [9]:

$$E_p^\parallel = E_p^\parallel \cos \alpha \left[ \sin \theta - r_p \sin (\theta + \delta_p) \right]$$

(2.11a)

$$E_p^\perp = E_p^\perp \sin \alpha \left[ \sin \theta + r_p \sin (\theta + \delta_p) \right]$$

(2.11b)

where $E_p^\parallel$ is the component parallel to the surface, $E_p^\perp$ is the component perpendicular to the surface, $E_p^\parallel \sin \theta$ is the incident electric field and $\theta$ is an arbitrary phase, $\alpha$ is the angle
of incidence measured with respect to the surface normal, \( r_p \) is the reflection coefficient, \( \delta_p \) is the phase change on reflection. \( \delta_p \) is nearly zero for small angles of incidence and 90 at grazing incidence, and 180 at 90 degree incidence. At small angle of incidence, \( \alpha \) is nearly zero, and \( E_{p\perp} \) is small. Although \( \cos \alpha \) is nearly one, \( E_{p\parallel} \) is small because the incident and reflected waves are in opposite directions and the vector sum is zero. At large angle of incidence, particularly at grazing incidence, there is an enhancement of \( E_{p\perp} \) along the surface normal. The absorbance, proportional to the ratio of the change in reflectance upon adsorption to total reflectance from clean surface (\( \Delta R/R \)), is a maximum when p light is brought in at grazing incidence to the crystal. As the angle of incidence approaches 90°, the (\( \Delta R/R \)) falls off again.

As described above, all molecules with a non zero dipole are capable of absorbing infrared radiation. However, when the dipole is adsorbed on a metal surface, an image dipole will be set up in the metal. If the dipole lies parallel to the surface, the net dipole moment will be zero, and infrared radiation will not be absorbed. If the dipole lies perpendicular to the surface, there will be an enhancement of the dipole moment and infrared radiation will be absorbed. This establishes the surface dipole selection rule for adsorbates on metal surfaces, which states that only those vibrationally active modes which have a dipole component normal to the surface will be excited (i.e. absorb radiation).

In FTIR, the infrared light from the source is split at the beam splitter. One beam is reflected off a stationary mirror, while the other is reflected off a moving mirror (Figure 2.7). The beams recombine on their path back and are detected at the mercury cadmium
Figure 2.7  Schematic diagram of the Michelson interferometer.
telluride (MCT) detector. The detector therefore sees a superposition of all this light which is called an interferogram. This interferogram is characterized by a large center burst when the path difference of each pair of coherent beams is zero and light of all wavelengths interfere constructively.

In a single beam FT-IRRAS spectrometer, one beam is reflected off a metal surface at high incidence angle before reaching the MCT detector. A He-Ne laser is also imaged onto the beam splitter. After reflecting off the stationary and moving mirror, the beams are recombined and the sinusoidal output is detected by a photo diode. In this way, the position of the scanning mirror is accurately measured. The computer uses the laser fringes to trigger the analog to digital converter (ADC) at precise intervals. The digitized interferogram is Fourier transformed to yield a plot of infrared intensity versus the wave number. The signal to noise ratio of the spectrum is limited by the signal to noise ratio of the interferogram. This in turn is limited by the dynamic range of the 16 bit ADC convertor. In short, the single beam experiment is digitizing noise limited.

2.8 Thermal Desorption Spectroscopy (TDS)

Thermal desorption of gases is a powerful probe of the chemistry and structure of a surface. Following adsorption, the sample is subjected to a heating cycle and the partial pressure of the desorbing species is monitored by a mass spectrometer. For high pumping speed and low heating rate, the measured partial pressure at a given time is proportional to the desorption rate. The time dependent desorption rate \( \mu(t) \) is proportional to the surface coverage and can be expressed as \([1, 10]\)
\[ \mu(t) = -\frac{dN}{dt} = v_n N^n e^{-E_d/RT} \]  

(2.12)

where \( N \) is the surface coverage, \( v \) is the frequency factor, \( n \) is the order of the reaction and \( E_d \) is the activation energy of desorption. Frequency factors lie between \( 10^{12} \) and \( 10^{15} \) s\(^{-1}\), with \( 10^{13} \) s\(^{-1}\) often chosen as a value for first order desorption.

The maximum desorption rate occurs at the temperature \( T_p \) (peak temperature) at which \( d\mu(t) / dt = 0 \) is satisfied.

For a first order (unimolecular) desorption process, the temperature at which the maximum desorption rate occurs is linearly related to the energy of desorption, and is independent of the initial adsorbate coverage on the surface. For a linear heating ramp (\( T = T_o + \beta t \), \( T_o \) is the starting temperature, \( \beta \) is the heating rate, \( t \) is the elapsed time), the following equation can be derived from eq. (2.12)

\[ \frac{E_d}{RT_p^2} = \frac{v_0}{\beta} \exp\left(-\frac{E_d}{RT_p}\right) \]

(2.13)

The activation energy of desorption may then be estimated from the peak temperature by using this equation.

For second order (bimolecular) desorption and a linear heating schedule, the temperature for peak desorption depends on the initial coverage \( \theta_o \), and

\[ \frac{E_d}{RT_p^2} = \frac{v_0}{\beta} \theta_o \exp\left(-\frac{E_d}{RT_p}\right) \]

(2.14)
$E_d$ and $v$ may be found following desorption measurements for several coverages.

For zero order desorption, the desorption rate is independent of surface coverage. The relation between $T_p$ and $E_d$ is

$$
\frac{E_d}{R} = \frac{v_0}{N_0} \beta \exp \left( -\frac{E_d}{RT_p} \right)
$$

(2.15)

The desorption peak shapes are useful for qualitative identification of reaction order. First order desorption peaks are asymmetric and the peak temperature is expected to be independent of the initial surface coverage. Even if the activation energy for desorption changes, the temperature at which desorption is essentially complete does not change. For second order desorption, the peak temperature decreases with increasing initial coverage and the peak is symmetric about the peak desorption temperature. In the case of zero order desorption, the peak temperature increases with increasing initial coverage.
References


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CHAPTER 3 OXYGEN DIFFUSION MEASUREMENTS

Zirconium alloys serve as the materials for pressure tubes in fuel channels in CANDU nuclear reactors. A zirconium oxide layer is grown on the pressure tubes to protect against the ingress of hydrogen (deuterium). If the hydrogen concentration in a portion of the tube exceeds the solubility limit, hydride can precipitate and eventually cause tube failure due to an increase in brittleness.

The measurement of oxygen diffusion in zirconium is important because over many years breakdown of the oxide can occur, which is most probably related to dissociation of the oxide and diffusion of oxygen into the bulk metal at the operating temperature of 573 K. Attempts have been made to model this process and related ones, thus giving rise to the need for accurate diffusion data [1], particularly at typical reactor operating temperatures of 573 K.

Much of the oxygen diffusion data in the literature is measured at high temperatures ( > 873 K) by using the conventional techniques such as microhardness, strain-aging, and internal friction [2, 3]. With the development of surface science, researchers now try to obtain quantitative diffusion parameters using surface sensitive techniques, such as XPS and AES [4]. This can be done by monitoring the dissolution of oxygen ad(ab)sorbed on the zirconium surface into the bulk. In practice unexpected discrepancies have been found between the diffusion parameters determined by conventional methods and those found from AES measurements. We shall argue that this arises because for the interpretation of the diffusion data obtained by surface sensitive
techniques, a model for the mass transport in the near-surface region is essential.

Although diffusion phenomena have been extensively studied since the end of the last century [5, 6] and many techniques have been employed by scientists to determine diffusion coefficients, a detailed theory for diffusion processes in the near surface region (which includes the diffusion process both inside the bulk and at the surface) has been rarely reported. This is mainly because diffusion is usually discussed in terms of a long-time process, therefore the details of the kinetics of diffusion in the near-surface region (usually several atomic layers) are negligible and therefore neglected in the analysis. Flinn et al [4] considered the deposited oxygen as an “ininitely thin oxygen layer” and used the classic Fick’s diffusion theory, to model the dissolution of the oxygen (referred as ITOL model). The oxygen diffusion coefficient obtained by using ITOL model is one magnitude lower than that in the literature [3].

We have developed a new theory for diffusion at the surface to explain our experimental AES data on oxygen dissolution at zirconium surfaces [7]. To model the diffusion in the near surface region, two issues must be taken into account: 1) the energy barrier for atomic motion at the surface is different from that inside the bulk; 2) the lateral interaction of the adsorbates, as the relative concentration of the diffusing elements at the surface is usually high. For oxygen dissolution from the zirconium surface, we controlled the oxygen coverage at about 0.5 ML, and the lateral interaction between oxygen atoms was found to be negligible [8]. We therefore neglect interactions between oxygen atoms in our model.

This chapter will show the major results of our diffusion model and its application
to the oxygen diffusion. Detailed information on the experiments, as well as the detailed mathematics of the model, can be found in Appendices I and II.

3.1 Diffusion Models

3.1.1 Basic equations

It was assumed that the disappearance of oxygen adsorbates from the surface into the bulk of the solid is controlled by the diffusion rate of the adsorbates. The dissolution process lasted only a few tenths of seconds at our experimental temperatures. Thus we are dealing with the initial stage, or "short time" behavior of the diffusion process. It has been shown, see for example [9], that when transport is measured over sufficiently small times and distances, the usual continuum description based on Fick’s law, must be replaced by a discrete hopping model.

In the discrete model we consider a semi-infinite solid in which the diffusing atoms migrate independently by nearest-neighbor hops between neighboring atomic planes which are each parallel to the surface of the crystal (Figure 3.1). The concentration gradient is in the direction perpendicular to these planes and the concentration is thus laterally homogeneous, a situation easily realized experimentally. Figure 3.2 illustrates the distribution of the energy barriers for migrating atoms. To simplify the problem, we assume that there are only two different energy barriers, one is for an atom leaving the surface ($E_0$), the other is for an atom jumping inside the bulk ($E$). The kinetic equations can now be written as:
Figure 3.1  The illustration of the arrangement of the atomic layers parallel to the surface layer ($n = 0$) in the discrete medium.
Figure 3.2  The energy barriers at the surface and inside the bulk. The surface is located at 0th atomic layer. $E_0$ is the energy barrier for an atom leaving the surface into the bulk. $E$ is the energy barrier for atom moving between layers inside the bulk.
\[
\frac{\partial c_0}{\partial t} = -zw_0c_0 + zw_1c_1 \\
\frac{\partial c_1}{\partial t} = -2zw_1c_1 + zw_2c_2 + zw_0c_0 \\
\frac{\partial c_n}{\partial t} = zw(-2c_n + c_{n-1} + c_{n+1}) \quad \text{(for } n > 2) 
\]

where \(a\) is the spacing of the neighboring planes, \(n\) is the distance of a plane from the surface plane in units of \(a\), \(c_n(t)\) is the concentration of the diffusing species at time \(t\) on the \(n\)'th plane, \(z\) is the number of sites on plane \((n + 1)\) accessible by one jump from a site on plane \(n\). The jump frequencies are \(w = A \exp(-E/kT)\) and \(w_0 = A_0 \exp(-E_0/kT)\), where the pre-exponential factors \(A, A_0\) and the activation energies \(E, E_0\) are assumed independent of temperature. The bulk diffusion coefficient for this model is

\[
D = wza^2 
\]

Our work uses AES to follow the time-dependence of the decrease of the O(KLL) signal as oxygen atoms diffuse away from a Zr single crystal surface into the bulk. The intensity of electrons emitted decays exponentially with increasing depth with a characteristic inelastic mean free path (IMFP), which depends primarily on the electron energy. The time dependent intensity \(I(t)\) versus time thus can be calculated from the summation over the concentration profile of the diffusing species with an exponential decay factor over all depths.
\[ I(t) = B \sum_{n=0}^{\infty} c_n(t)e^{-ix_n} \]  

(3.3)

where \( s = \lambda/cos\alpha \), \( \lambda \) is the IMFP of the O(KLL) electrons [11.5 \, \text{Å} \ [10]], \( x_n = n\alpha \), \( \alpha \) is the electron collection angle measured with respect to the surface normal (42°), and \( B \) is a constant of proportionality. (we omit the constant \( B \) for convenience in subsequent equations). The solution of equations 3.1 subject to the initial condition

\[ c_0(0) = f \]  

\[ c_n(0) = 0 \]  

\( (n > 0) \)  

\( (n = 0) \)

then yields [7]

\[ I(t) = fe^{a_{1,1}t} \left[ 1 - b\beta_1 \int_0^t dy \left[ I_0(by) + I_1(by) \right] e^{-(1 \cdot \alpha_1)by} \right] \]  

\( (W = 0) \)  

(3.4a)

\[ I(t) = fe^{a_{1,1}t} - \frac{\beta_1}{\alpha - \alpha_1} \left( e^{a_{1,1}t} - e^{a_{1,1}t_1} \right) + \frac{\beta_1}{\alpha - \alpha_1} \int_0^t dy \left[ I_0(by) + I_1(by) \right] e^{-by} \left[ e^{ab(t-y)} - e^{a_{1,1}(t-y)} \right] \]  

\( (W \neq 0) \)  

(3.4b)

where \( f \) is the initial amount of the deposited oxygen, \( I(t) \) is the modified Bessel function, \( b = 2I/\alpha' \), so that \( bt \) is a dimensionless time, \( W = (w - w_0)/w, \alpha = (1 - W)^2/2W, \beta = (1 - W)/2W, \alpha_1 = (e^{\omega u} + e^{\omega u} - 2)/2, \beta_1 = [W(e^{\omega u} - 1) + (e^{\omega u} - 1)]/2. \)

3.1.2 Explanation of the parameters

The surface effect is represented by the parameter \( W \), which has the following physical properties:
i) $W < 0$, i.e. $w_o > w$, $E_o < E$, the surface repels the solute atoms from the surface layer. These species accumulate at the layer beneath the surface and act as the limiting factor in the diffusion of these species into the bulk.

ii) $1 > W > 0$, i.e. $w_o < w$, $E_o > E$, the surface has a tendency to hold the atoms. As the atoms are held at the surface, a depleted region is formed just beneath the surface. A consequence of some importance for this situation is that if the initial sample condition has the solute distributed homogeneously through out the bulk, solute segregation at the surface can occur.

iii) $W = 0$, i.e. $w_o = w$, $E_o = E$, the surface shows the same behavior as the bulk.

iv) $W = 1$, i.e. $w_o = 0$, $E_o = \infty$, the surface becomes a sink to hold the atoms and a surface compound may be formed.

3.1.3 The distribution of the deposited element at different times

Figure 3.3 is a schematic illustration at four times of the distribution of the deposited element in the near surface region for three different choices of $w_o / w$. The initial concentration $f$ is taken to be unity. For the case of $E_o > E$ ($w_o / w < 1$), the atom is trapped at the surface, and the dissolution of the deposited element is slower. With increasing time, a depleted region appears beneath the surface. For the case of $E_o < E$ ($w_o / w > 1$), the deposited element is repelled from the surface. But instead of dissolving into the bulk, an enriched region appears beneath the surface.

3.1.4 The dissolution rate of the deposited elements

Figure 3.4 shows the decrease of the attenuated intensity $I$ with time as predicted by equation 3.4. The variation of behavior with the parameters $W$ is qualitatively what
Figure 3.3  The distribution of the deposited element at different times
Figure 3.4  The variation in dissolution rate of surface species due to the different surface energy barriers. These curves are computed from equations 3.4.
would be expected, i.e. as compared with $W = 0$ (no surface effect) the decay is slower for $0 < W < 1$ and is faster for $W < 0$.

Figure 3.5 shows the comparison of the rate of decrease of attenuated intensity $I$ vs dimensionless time $bt$ for the conventional continuum diffusion theory and for discrete diffusion theory assuming no surface effect ($W = 0$). It can be seen that the two models show a significant difference at $bt < 10^3$, with the diffusion process predicted by the discrete model being slower than that predicted by the continuum model. It is therefore not surprising that the discrete model will yield larger diffusion coefficients than the continuum model if they are both used to fit to the same set of data. For oxygen diffusion in zirconium, the diffusion coefficient is between $10^{-21} - 10^{-15}$ cm$^2$/s at 473 K to 673 K [3]. The interlayer spacing in zirconium is of the order of $10^{-4}$ cm. Then $b = 2D/a^2 = 10^{-3}$ to $10^{-1}$ s$^{-1}$ for this case. In our experiment, the measurement time is from $t = 0$ to 100 seconds, and therefore $bt = 10^{-3}$ to 1000. This is in the range of "short time" behavior (Figure 3.5) and confirms that our data must be described by the discrete diffusion theory.

3.2 Dissolution of the adsorbed oxygen

3.2.1 Isothermal measurements

To apply our model, we employ equation 3.4 to fit our data (Figure 3.6). In order to find the proper $W$ value, polynomial fits for $I(t)$ against $bt$ were determined for a series of different $W$ values through equation 3.4b. The experimental data are then fitted to these polynomial expressions and a series of diffusion coefficients $D$ are obtained for these $W$'s. The fitting error $Err$, the square root of the sum of squares of the residuals, is also
Figure 3.5  Comparison of the continuum and discrete diffusion theory without inclusion of the surface effects. The discrete theory reduces to continuum theory when dimensionless time $bt > 1000$. It shows the difference at "short time", $bt < 1000$. 
Figure 3.6  The decrease of $O(KLL)$ intensity due to the dissolution of oxygen at selected temperatures. The dots are the experimental data while the curves are results from fitting to equation 3.4. a) Zr(1010), b) Zr(0001)
determined in each case. Figure 3.7 is a typical plot for the change of $D$ and $Err$ for different values of $W$. We can see that the best fit is obtained within a range of $W\ (\pm 0.5\ )$, therefore the $D$ we obtain does not have a single, unique value but is reliably determined within some error limits in a certain range. The results of this fitting procedure are plotted as the open data points in Figure 3.8. The diffusion coefficients so derived are smaller than those obtained without allowance for the effect of the surface potential well (closed data points), and closer to the literature values [3] (see Figure 3.8). The relationship of $W$ to temperature, $T$, is shown in Figure 3.9. The resulting Arrhenius expressions for the diffusion coefficient of oxygen now are:

for Zr(0001) \[ D^{(1)} = 0.115 \exp(-44.45 \text{kcal/RT}) \text{ cm}^2/\text{s} \] (3.5a)

for Zr(10\bar{1}0) \[ D^{(2)} = 1.07 \exp(-46.18 \text{kcal/RT}) \text{ cm}^2/\text{s} \] (3.5b)

here we use the superscript $1$ and $2$ to indicate the (0001) and (10\bar{1}0) surfaces, respectively. Assuming that the pre-exponential factors for the jump frequencies $w$ and $w_\phi$ are approximately equal, the energy barrier at the surface can be calculated by the equation

\[ E_\phi = E - RT \ln(1 - W) \] (3.6)

The value of $(E_\phi - E) / R$ can be obtained from the slope of the line of $\ln(1 - W)$ vs $T^{-1}$ shown in Figure 3.9. We obtain surface energy barriers of $E_\phi^{(1)} = 43.54 \text{ kcal}$, $E_\phi^{(2)} = 45.65 \text{ kcal}$, which are 97.97% and 98.87% of the energy barrier for atom moving inside the bulk. The effect of the surface is not strong in this system.

3.2.2 Continuous heating methods

The observation of the dissolution of the absorbates during heating eliminates the
Figure 3.7 The fitting error, $Err$, at different values of $W$. 
Figure 3.8  Diffusion coefficients from  a) Ritchie & Atrens [3] (dotted line), b) ITOL model of FZN [4] (dashed line), c) our model without inclusion of surface effects (closed circles and triangles); d) our model with inclusion of the surface effect (open circles and triangles). The linear fits to the data in d) are shown as the solid lines.
Figure 3.9  
The relationship of the surface factor $W_s$ and temperature, $T$. The slope of the line for $\ln(1 - W_s)$ vs $1000/T$ yields the difference between the diffusion energy barriers for the surface and the bulk.
errors which result from the ramp-and-hold heating method, such as temperature overshoot and oxygen loss during the heating process [11]. Moreover, it is much easier to implement experimentally. For this purpose, we define the average frequency of hops as

\[
\overline{w} = \frac{1}{\tau} \int_{0}^{\tau} w(t') dt'
\]  
(3.7)

By following a similar procedure we obtain, for the model without the surface effect \((W = 0)\),

\[
I(t) = \int e^{\frac{\alpha T t}{r}} \left\{ 1 - b \beta_1 \int_{0}^{t} dy[I_0(\bar{b}y) + I_1(\bar{b}y)] e^{-\frac{1}{2} \alpha T r} \right\}
\]  
(3.8)

where \(b = 2\bar{w} = 2\overline{D}/\alpha T\) and \(D\) is the average diffusion coefficient over the period of time \(t\). Equation (3.8) allows one to calculate \(I(t)\) for a given value of \(bt\) and so construct a polynomial fit for \(bt\) as a function of \(I(t)\):

\[
\bar{b}t = \sum_{k=0}^{n} a_{k} I^{k}(t)
\]  
(3.9)

For a linear heating rate \(\gamma\) (i.e., \(T = T_{0} + \gamma t\) or \(dT/dt = \gamma\)), we have

\[
D(T) = \frac{a^{2} \gamma}{2} \sum_{k=0}^{n} k a_{k} I^{k-1} \frac{dI}{dT}
\]  
(3.10)

The relationship between \(I\) and \(T\) and between \(dI/dT\) and \(T\) can be determined from experimental results, Figure 3.10. An Arrhenius plot of the diffusion coefficients
Figure 3.10  AES data for dissolution of oxygen during a linear temperature ramp.
determined in this way is compared with the results from the ramp-and-hold experiments in Figure 3.11. The analyses of both types of experiment neglect any possible surface effect \( w = w_o \). It is clear that the result from the analysis of the continuous heating data is quite consistent with the data obtained from the ramp-and-hold experiments without inclusion of the surface effect.

3.3 Dissolution of the oxide film

It is known that oxide will dissolve into bulk Zr when the sample is heated to high temperature. In order to examine the major factor controlling oxide dissolution (oxide dissociation or oxygen diffusion into the \( \ldots \) ), an isothermal heating experiment was performed.

Figure 3.12 shows schematically the oxide dissolution process on Zr. If the dissolution of oxide is controlled by diffusion of oxygen in the bulk, from Fick's law, the distribution of oxygen in the bulk will be:

\[
c(x, t) = c_s \left[1 - \text{erf}(x/2(Dt)^{0.5})\right] \tag{3.11}
\]

where \( c_s \) is the oxygen concentration at the metal-oxide interface, (which is 29% \( \text{a/a} \) from the phase diagram [12]), \( t \) is the experimental time and the origin of \( x \) is always taken at the interface, \( \text{erf}() \) is the error function. The flux of oxygen atoms can then be expressed by

\[
J(x, t) = c_s(D/x^2) \exp(-x^2/4Dt) \tag{3.12}
\]

The number of oxygen atoms per unit area dissolved from the oxide into the bulk is given by:
Figure 3.11  Comparison of the diffusion coefficients obtained by heating (lines) and ramp-and-hold experiment (symbols): a) Zr(0001) (circle and dotted line); b) Zr(1010) (triangle and dash-dotted line); c) reference [3] (dashed line). The calculation does not include the surface effect.
Figure 3.12  Schematic illustration of model: (a) initial condition $(t = 0)$, (b) during the dissolution of ZrO$_2$ film. $C_o$ is the oxygen concentration in ZrO$_2$. $C_s$ is the solubility of oxygen in Zr. Zr(O) is the Zr containing oxygen.
\[ M(t) = 2 \, c_0 (Dt/\pi)^{0.5} \]  

(3.13)

The diffusion coefficient can be obtained from the plot of \( M(t) \) vs. \( t^{0.5} \). If the rate controlling factor is the diffusion of oxygen in Zr, the diffusion coefficient should be consistent with the published results.

The isothermal dissolution of oxide experiment was performed in the following manner. First, the Zr sample was exposed to oxygen at 90 K for 20 L. An oxide film of thickness of 12.4 Å was well established from the NRA and AES results [13]. The sample was then rapidly heated, at a rate of 100 K/s to the chosen temperature and then held at that temperature. The Auger signals of zirconium and oxygen were recorded during the entire experiment. The thickness of oxide could be obtained from the Auger signals [13].

Six temperatures, 573, 623, 648, 673, 698, and 723 K, were chosen for the isothermal oxide dissolution experiments. Figure 3.13 illustrates \( M(t) \), the quantity of oxygen dissolved into the bulk, vs annealing time. The oxygen diffusion coefficients were calculated by using equation (3.13). They are compared with the diffusion results of Ritchie and Atrens [3] in Figure 3.14. The good agreement indicates that the diffusion of oxygen into the bulk is the major rate controlling factor for the dissolution of oxide.

### 3.4 Summary

We have developed experimental methods and an appropriate discrete mathematical model to permit the determination of the diffusion coefficient of oxygen in zirconium at rather low temperatures. The method itself is not just limited to this specific system and has the potential to be applied to other systems. We found that the zirconium
Figure 3.13  quantity of oxygen dissolved into the bulk from the oxide vs annealing time at six temperatures: (1) 573 K; (2) 623 K; (3) 648 K; (4) 673 K; (5) 698 K; (6) 723 K.
Figure 3.14  Comparison of the diffusion coefficients of oxygen from [3] (dashed line) and the value derived from the dissolution of the oxide (dark dots).
surface does not exert a very strong effect on the dissolution of the oxygen in the temperature range 473 K to 673 K. An earlier discrepancy between the diffusion coefficients obtained for oxygen by conventional and AES methods is diminished in our new method. Results of the oxide dissolution experiments indicate that the dissolution of the zirconium oxide is controlled by oxygen diffusion into the bulk.
References


[7] see APPENDIX I


[13] See APPENDIX II
CHAPTER 4 HYDROGEN ADSORPTION AND SEGREGATION

It has been found that two types of major failure determine the longevity of components made from Zr and its alloys: 1) delayed hydride cracking controlled by stress gradients around a flaw, and 2) a rapid cracking process through hydride "blisters" formed around a "cool" spot at the surface [1, 2]. These failures are related to the formation of hydride, and hence the bulk concentration of hydrogen. The hydrogen source in the nuclear reactor operating environment could be from ingress of hydrogen from corrosion and other interfacial processes, as well as the segregation of impurity hydrogen from inside the bulk of the Zr-alloy component.

Only a few publications have been found concerning the formation of hydrides, both by adsorption and segregation, in the H-Zr system, especially at the operating temperature of a Candu nuclear reactor (~ 583 K). The kinetics of adsorption of hydrogen on a zirconium surface is a complex system in which at least three processes can occur simultaneously: adsorption, hydriding and dissolution. For segregation, the hydrogen state on the Zr surface is also the result of a balance among segregation, hydriding and dissolution.

In this work, we used surface science techniques, such as NRA, SSIMS, AES, and $\Delta \phi$ to study the adsorption and segregation of hydrogen in zirconium. A mathematical model was established to interpret the adsorption kinetics of hydrogen with consideration of these effects.
4.1 Hydrogen adsorption

4.1.1 Adsorption kinetics

Figure 4.1 shows the typical uptake kinetics of D$_2$ on a Zr(1010) surface measured by NRA for various exposures up to 10 L at 100, 293 and 370 K. The results show that the measured hydrogen concentrations increase most rapidly at low exposures at 100 K, then attain a constant value at exposures above 1 L. Similar behavior is observed at 370 K. The concentration of hydrogen also increases rapidly at low exposures at 293 K, but no saturation is observed in the experimental range of exposure ( < 10 L ).

It is known that the sampling depth of NRA is about 0.5 μm [3]. If the ad(ab)sorbed D does not migrate further away from the surface than this distance (such as at 100 K), the concentration results measured by NRA would be equivalent to the total hydrogen uptake. However, if the D migrates a significant distance relative to the NRA sampling depth during the exposures (such as at 370 K), the D measured by NRA is just a fraction of the total uptake. Table 4.1 lists the diffusion length for hydrogen along the <1010> direction for 100 sec, the typical D$_2$ exposure time during the experiment.

The initial sticking coefficient at 100 K is found to be 1.0. It remains almost constant up to exposures of ~ 0.5 L, above which the surface appears to become inactive towards hydrogen. The saturation concentration of hydrogen is 9.10 x 10$^{14}$ atoms/cm$^2$, equal to the surface atomic density of Zr(1010) of 9.04 x 10$^{14}$ atoms/cm$^2$. Since the adsorbed hydrogen cannot diffuse below the surface, we might reasonably postulate the atomic ratio of hydrogen to zirconium on the surface is one to one.

The uptake curve at 370 K shows a similarity to that of 100 K, but the mechanism
Figure 4.1  Uptake of hydrogen on the Zr(10̅10) surface measured by NRA (²H(²He,p)⁴He reaction) at 100 K (circles), 293 K (squares) and 370 K (triangles). The lines through the data points are polynomial fitting curves. The curves and fitting procedures utilize data (not illustrated) at exposures > 10 L.
Table 4.1  The diffusion length of hydrogen along the Zr \(<10\bar{1}0>\) direction at 100, 293 and 370 K

<table>
<thead>
<tr>
<th></th>
<th>100 K</th>
<th>293 K</th>
<th>370 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient (D*, mm²/s)</td>
<td>8.7x10⁻²¹</td>
<td>4.48x10⁻⁸</td>
<td>1.05x10⁻⁶</td>
</tr>
<tr>
<td>diffusion length** (μm)</td>
<td>9.33x10⁻⁶</td>
<td>2.11</td>
<td>10.2</td>
</tr>
</tbody>
</table>

* The diffusion rate: \(D = 0.173\exp(-8887\text{cal. mol}^{-1}/RT)\) mm²/s [6]
** The diffusion length: \((Dt)^{0.5}\), \(t = 100\text{sec.}\)
is totally different. At 370 K, the adsorbed D on the Zr surface can diffuse very rapidly into the bulk at higher coverages. An equilibrium is established among adsorption, dissociation and dissolution. Although it seems that D is saturated at 1.5 L, the total uptake of the D increases steadily as the adsorbed hydrogen does not stay at the surface and can diffuse deep into the bulk [4]. The total uptake \( U_t \) is the sum of the surface and bulk uptakes, and can be expressed as

\[
U_t = \left(1 + L(t) / [a \alpha(\theta_s)]\right) \theta_s
\]

(4.1)

where the diffusion length \( L(t) = (Dt)^{1/2} \), \( \theta_s \) is the surface uptake and can be measured by SSIMS, \( a \) is distance between the atomic layers parallel to the surface, \( D \) is the diffusion coefficient in the bulk, \( \alpha(\theta_s) \) is the surface equilibrium constant corresponding to a given value \( \theta_s \). (A detailed discussion on this model can be found in reference [4]). Figure 4.2 is a schematic illustration for this process. At a lower temperature, the diffusion length is very small, and the bulk uptake can be neglected (see curve for 100 K in Figure 4.1). The large diffusion length at the higher temperature, which leads to a large bulk uptake, may also result in the distribution of the absorbed element over a long distance. Therefore, the measurable uptake by NRA originates mainly from the surface, which approaches equilibrium very early in the exposure (see curve 370 K in Figure 4.1). At a temperature where the diffusion length is comparable to the NRA sampling distance, such as 293 K in this experiment, bulk uptake is established constantly and most is distributed within the NRA sampling distance. Thus the uptake measured by NRA keeps growing, as shown in Figure 4.1.

With SSIMS, the concentration of D present only in the surface layer can be
Figure 4.2  Schematic illustration of the NRA measurement on the D uptake on zirconium surface. The total uptake ($U_t$) = surface uptake ($U_s$) + bulk uptake ($U_b$), and the NRA measured D uptake $U_{NRA} = U_s + \alpha U_t$ ($0 < \alpha < 1$), where $\alpha U_t$ is the bulk uptake within the NRA sampling distance. At $T > 340$ K, $U_t \approx 0$, so $U_{NRA} = U_s$. At $T = 370$ K, $\alpha = 0$, so $U_{NRA} = U_s$. At $T = 293$ K, $\alpha \neq 0$, $U_t \neq 0$, therefore $U_{NRA} = U_s + \alpha U_t > U_s$. 

NRA sampling depth (0.5 µm) 

hydrogen atoms
determined. SSIMS was calibrated by the following procedure. First, NRA was used to
determine the uptake of D₂ on the Zr surface at 293 K. Then the uptake was also
measured by SSIMS (D⁺) under exactly the same exposure conditions (temperature and
pressure). The result is shown in Figure 4.3. It can be seen that the form of the D⁺ yield
with exposure exactly matches the absolute coverage obtained by NRA when the coverage
is below $8.2 \times 10^{14}$ atoms/cm². Above this coverage, the NRA signal continues to increase
but the SSIMS signal remains constant. Because of the excellent match between the NRA
and SSIMS results below $8.2 \times 10^{14}$ atoms/cm², we can conclude that the D⁺ ions yield in
our SSIMS experiment is accurately and linearly proportional to the surface concentration
of hydrogen, from which a proportionality constant can be derived. This conclusion is
especially useful when we use SSIMS to measure the kinetics of D segregation which will
be discussed in section 4.2.

4.1.2 Adsorption Chemistry

The electronic structure of zirconium hydride has been extensively investigated
experimentally and theoretically in the last decade [5 - 8]. It has been found that the
hydrogen atom acts as an electron acceptor and zirconium atom as an electron donor in
the hydride. More importantly, a new photoemission peak was found below the Zr Fermi
level 6.3 - 7.0 eV (denoted as $V_h$) [5 - 8]. It was confirmed that this s-like peak is related
to the orbital associated with the zirconium-hydrogen bond.

The dominant Auger peaks related to the valence band in zirconium metal are: the
N₁N₂V peak at 23 eV, the M₄,5N₁V at 127 eV, the M₄,5N₂V peak at 146 eV and the
M₄,5VV peak at 178 eV. (These kinetic energies are referred to the energies of Auger
Figure 4.3 Comparison of hydrogen uptake measured by NRA and SSIMS at 293 K
lower peaks in the differential spectrum). The energy of valence band electron (V) in zirconium metal is about 1 eV below the Fermi level. The binding energies of core level electrons in the hydride shift 0.7 to 1.0 eV towards higher values, with little difference from level to level. The contribution of the energy shifts of the core level electrons to the energy difference between V and V_h related Auger signals will be very small. Therefore the NiN2V_h, M45N1V_h, M45N2V_h and M45V_hV_h Auger electrons will have about 5.3 - 6.3 eV lower kinetic energy than N1N2V, M45N1V, M45N2V and M45VV Auger electrons, respectively. Due to the appearance of the V_h, it is possible to examine the formation of hydride more precisely (through the zirconium-hydrogen s-like bond) by monitoring the Auger signals which are related to the V_h.

Figure 4.4 shows the AES spectra taken on the Zr(10\(\overline{1}\)0) surface for various hydrogen exposures at 100 K. It is apparent that new peak features appeared in the energy regions below single valence band related Auger peaks about 5.5 eV, and that below double valence band related Auger peaks 5.5 - 11 eV, at all stage of exposures. The most dominant V_h related peak is the NiN2V_h peak at 17.5 eV, which is due to the NiN2V Auger transition having the highest cross section among all Auger transitions. These new peaks apparently indicated that the electron orbitals associated with zirconium-hydrogen bonds have been formed upon the hydrogen exposures. Moreover, the energies of these peaks seem to be constant at all hydrogen exposures. This indicates only one type of bond is formed. It is difficult to conclude that a hydride has been formed, because we don't know whether the chemisorption bond is the same as that in the hydride.

Figure 4.5 shows the work functions measured during hydrogen exposure at
Figure 4.4 Auger spectra from the Zr(10\bar{1}0) surface for various hydrogen exposures at $T = 100$ K. All the spectra have been normalized against the clean surface.
Figure 4.5  The change of work function, $\Delta \Phi$, during hydrogen exposure at 100, 150, 293, 370 and 450 K
various temperatures. It can be seen that the work functions at various temperatures have a tendency to a constant value after certain hydrogen exposures. Comparing the results in Figure 4.5 with those in Figure 4.1, it was found that the exposures where the constant $\Delta \phi$ are reached are about the same as where surface saturations are attained. This indicated that when the hydrogen is saturated on the surface, its movement also stops. An exception is that the $\Delta \phi$ at 293 K becomes constant at $> 6$ L, higher than the exposure at which the hydrogen coverage is saturated (1.5 L), which indicates that some migration of hydrogen atoms must occur after surface saturation is reached.

The saturation work function at 100 K is $+ 75$ mV. With increasing exposure temperatures, the values of the saturation work functions decrease until at temperatures approaching 370 K, the saturation $\Delta \phi$ reaches a minimum of $- 60$ mV. The different signs of the saturation $\Delta \phi$ values indicate that adsorbed hydrogen after saturation prefers to stay above the surface at lower temperatures and below the surface (in the subsurface region) at higher temperatures. The temperature dependence of $\Delta \phi$ is also seen in an annealing experiment where the zirconium surface was exposed to hydrogen at 100 K for 2 L to get the saturated coverage and the $\Delta \phi$ was then measured during linear heating of the sample at a rate of 1 K/s (Figure 4.6). The $\Delta \phi$ decreases dramatically between 100 to 230 K and then reaches the minimum at 370 K, which indicates the hydrogen located above the surface has moved into the subsurface region with increasing temperature. These temperature dependence behaviors indicated that there are (at least) two appropriate sites on the Zr(1010) surface for the residence of hydrogen, one above the surface and another in the subsurface region.
Figure 4.6  The change of work function on Zr(10\bar{1}0) surface during linear heating (1 K/s). The sample was exposed to hydrogen for 2 L at 100 K before the heating.
4.2 Hydrogen segregation

4.2.1 Segregation kinetics

Figure 4.7 shows the experimental results of hydrogen segregation on Zr(0001) and Zr(10\bar{1}0) surfaces measured by SSIMS during linear heating. It can been seen that the segregated hydrogen can be detected at 350 K on Zr(10\bar{1}0) and at 420 K on Zr(0001). The surface concentration increased exponentially with increasing temperature in the initial stages as the rate of segregation in the lower temperature region is controlled by the diffusion rate of hydrogen in the bulk. The fact that the temperature at which the segregation started is lower on Zr(10\bar{1}0) than on Zr(0001) can be understood by the diffusion rate along the <10\bar{1}0> direction being faster than along the <0001> direction. With a further increase in temperature, the \emph{net} segregation rate starts to decrease and a maximum in surface concentration of hydrogen is observed. Above this temperature, the surface concentration of hydrogen decreases due to the dissolution of segregated hydrogen back into the bulk.

The heat of segregation is dependent on the release of elastic strain introduced by dissolved segregant in the bulk, bonding with the free bonds of the substrate atom on the surface and the formation of surface compounds. Hydrogen atoms dissolved in Zr prefer tetrahedral interstitial sites. The heat of hydrogen segregation originates mainly from the bonding between segregated hydrogen atoms with Zr atoms on the surface or from formation of a surface Zr-H compound. If the heat of segregation is dominated by the bonding with the free bonds of Zr atoms on the surface, the free bonds on these two surfaces are different, which may result in different heats of segregation. This is not the
Figure 4.7  Surface segregation of hydrogen on Zr(0001) and Zr(10\bar{1}0) measured by SSIMS during linear heating \(\sim 1 \text{ K/s}\).
case here [11], and therefore, it is possible that hydride-like products are formed on both surfaces, to give similar heats of segregation.

4.2.2 Diffusion process in hydrogen segregation

Since the segregation rate in the initial stage is controlled by bulk diffusion of segregant atoms, the bulk diffusion parameters can be derived from the segregation rate in this region. A well known equation to describe the relationship between bulk diffusion and surface segregation at a constant temperature was proposed by Mclean [10]. In the initial stage of segregation, this relationship can be expressed as

$$
\theta_i = 2(Dt / \pi a^2)^{1/2} \theta_s
$$

(4.4)

where $\theta_s$ is the concentration of the segregant in the bulk. The diffusion coefficient can be obtained from the slope of curve of $\theta_i$ versus $t^{0.5}$.

Figure 4.8 shows the heating and cooling schedule used for diffusion measurements and the corresponding changes of surface concentration of hydrogen during heating and cooling. After being held at 920 K for two minutes (where all of the surface hydrogen has dissolved into the bulk), the sample was rapidly cooled to one of the desired temperatures and held. SSIMS measurements of the surface concentration yielded a linear relationship for $\theta_s$ versus $t^{0.5}$, as shown in Figure 4.9. Similar experiments were also performed on the Zr(0001) surface. The bulk diffusion coefficients along $<0001>$ and $<10\bar{1}0>$ are shown in Figure 4.10. The extrapolation line from results obtained on polycrystalline Zr at higher temperatures by the conventional methods are also plotted for comparison [9].

It is shown in Figure 4.10 that the diffusion of hydrogen in Zr is highly anisotropic:
Figure 4.8  Hydrogen segregation on Zr(10\text{1}0) measured by SSIMS during annealing at eight temperatures.
Figure 4.9  H⁺ yields versus the square root of the annealing time. The linear relationship was observed during the initial stage of segregation.
Figure 4.10  The diffusion coefficients of hydrogen along the $<0001>$ and $<10\bar{1}0>$ directions. The dashed line is an extrapolation of published results at higher temperature for polycrystalline Zr.
\[ D = 0.173 \exp(-8887/RT) \text{ mm}^2/\text{s} \text{ along } <10\bar{1}0>, \] which is faster than along <0001>, where 
\[ D = 0.034 \exp(-9565/RT) \text{ mm}^2/\text{s}. \] This is mainly because that the activation energy for hydrogen motion is higher along <0001> than <10\bar{1}0>. It is known that diffusion of hydrogen in Zr follows an interstitial diffusion mechanism. The atomic density on the (0001) face \((1.11 \times 10^{15} \text{ atoms/cm}^2)\) is almost twice of that on the (1\bar{1}0) face \((6.0 \times 10^{14} \text{ atoms/cm}^2)\), which provides less space to let hydrogen pass through (0001) than (1\bar{1}0). Therefore, the activation energy is higher in the <0001> direction, 9565 kcal/mol, than along <10\bar{1}0>, 8887 kcal/mol. The activation energies are even lower in polycrystalline Zr, as there are a lot of short diffusion paths provided by the grain boundaries and defects. This may result in the higher diffusion coefficient of hydrogen in polycrystalline zirconium.

### 4.3 Summary

AES results indicate that the bond between hydrogen atoms and surface atoms of zirconium is energetically similar to that in zirconium hydride. Work function measurements indicate the presence of two types of adsorption site, one above the surface and another in the subsurface region. Hydrogen is more strongly bound at the subsurface sites than in those above the surface, but no visible difference of electronic structure was found by AES.

It was found that hydrogen has a very strong tendency to segregate on these surfaces of Zr. The diffusion coefficients of hydrogen along the <0001> and the <10\bar{1}0> directions in single crystal zirconium were measured by the kinetics of surface segregation. It was found that the diffusion along <0001>, \[ D = \sqrt{0.034 \exp(-9565/RT)} \text{ mm}^2/\text{s}, \] is lower
than that along $<10\bar{1}0>$, $D = 0.173\exp(-8887/R7) \text{ mm}^2/\text{s}$. This may be explained by the
different atomic densities on $(0001)$ and $(10\bar{1}0)$ faces, which affect the activation energy
for diffusion.
References


[4] See APPENDIX III.


CHAPTER 5 ADSORPTION AND DESORPTION OF WATER

As stated in the previous chapters, hydrogen, either deliberately added or present as a result of radiolysis or corrosion reactions, may diffuse into the bulk of the zirconium alloy components, from where it can precipitate as hydride, possibly causing delayed hydride cracking (DHC) at high temperatures. The desire for an improved understanding of the mechanisms of hydrogen ingress led to the present study of the interaction of D$_2$O with zirconium. This is also a very interesting system in its own right, since Zr is very reactive and can readily dissolve the possible reaction products, O and D (see Chapter 3 and 4).

Very few papers have been published in this area. Zeheringer et al. [1] studied the adsorption of water on polycrystalline Zr by photoemission experiments and found that the first adsorbed layer of water dissociated into adsorbed oxygen (O$_{ads}$) and hydrogen (H$_{ads}$) and/or (OH)$_{ads}$ and H$_{ads}$ at 100 K. This experiment was really only a reference study for research on the adsorption of water on amorphous Ni$_{64}$Zr$_{36}$. To the authors’ knowledge, no other well controlled studies on water-zirconium system have been published.

This chapter shows the major results of our study on the interaction of water with zirconium surface. The detailed results, as well as the experimental methods, can be found in Appendix V.
5.1 Kinetics of adsorption and desorption

5.1.1 NRA determination of coverage

NRA was used to measure the coverage produced by the capillary doser under standard conditions (constant pressure in the doser source) for a chosen exposure in seconds. The coverage attained in 100 s by backfilling the chamber to \(1 \times 10^8\) Torr \(D_2O\), (which produces a 1 Langmuir exposure, 1 L, where 1L = \(1 \times 10^6\) Torr·s) was also measured. By comparing the absolute coverage produced by these two methods, the localized \(D_2O\) pressure at the Zr(0001) achieved using the capillary doser can be determined.

Figure 5.1 shows the NRA results achieved using the capillary doser. The absolute coverage of \(D_2O\) should be the same as the oxygen coverage, but half of the deuterium coverage (measured as D, not \(D_2\)) provided no selective desorption of O or D occurs. By comparing the dosing rates using the capillary and background dosing methods, we established that: i) 1 s capillary dosing produced 0.0052 ML of D on Zr(0001); ii) background dosing produced a D-coverage of 0.90 ML (1 ML = 1 monolayer = \(1.11 \times 10^{15}\) D cm\(^{-2}\)) for an apparent exposure of 1 L \(D_2O\). Figure 5.1 shows that 200 seconds of capillary dosing produces 1.04 ML of D, which is equivalent to \(1.04/0.90 = 1.16\) L of exposure. The local pressure at the sample while using the capillary doser is thus \(1.16 \times 10^{-4}/200 = 5.8 \times 10^{-9}\) Torr. When corrected for background pressure, the local water pressure at the sample is about \(5.3 \times 10^{-9}\) Torr for these conditions which could be readily reproduced. This result was confirmed by comparing \(\Delta\phi\) during \(D_2O\) exposure using the capillary dosing, with that produced by raising the ambient pressure to \(5.8 \times 10^{-9}\)
Figure 5.1  The absolute coverage of D and O on Zr(0001) against the D$_2$O exposure determined by NRA. Filled circles: D-coverage ($^3$H($^3$He,p)$^4$He reaction); filled squares: O-coverage ($^{16}$O($^2$H,p)$^{17}$O reaction). The solid line is the linear fit of the D-coverage vs exposure. The dashed line is half of the deuterium coverage, which should be equal to the coverage of oxygen in principle if the surface stoichiometry is D$_2$O. Bottom axis: D$_2$O dosing time by using capillary array. Top axis: calibrated exposure in Langmuir, L.
5.1.2 TDS characterization of D$_2$O adsorption

Figure 5.2a shows the thermal desorption spectra of mass 20 (D$_2$O) after different D$_2$O exposures at 80 K. No D$_2$O desorption was found when the D$_2$O exposure was less than 90 seconds. We term the adsorbed layer formed below the critical exposure of < 90 s the "chemisorbed layer". At D$_2$O exposures greater than or equal to 90 seconds, a thermal desorption peak occurs at 178 K which increased in intensity with increasing D$_2$O exposure. A second peak, centered at 163 K, was first detected as a shoulder on the first peak, when the D$_2$O exposure was greater than 200 seconds. With further exposure, the intensity of the 163 K peak increased steadily without saturation, while the 178 K peak tended to saturation (see Figure 5.3). Given that no water desorption can be detected for exposure of < 90 s, and that the 178 K peak can be saturated, we attribute it to desorption of D$_2$O from a second adsorbed layer; the 163 K peak then arises from an ice layer. This structure of the adsorbed water layers is schematically illustrated in Figure 5.4. By converting the capillary doser time to the absolute coverage using the NRA results, we can establish: i) a chemisorbed layer, which occurs during the first 90 s (or 0.23 ML, or 0.52 L); ii) a second adsorbed layer, which starts at 90 s and saturates at 260 s (or 0.67 ML, or 1.5 L); iii) an ice layer, which starts to build up at 200 s (or 0.51 ML, or 1.14 L) and of course never saturates.

Figure 5.2b shows the desorption of D$_2$ during heating after D$_2$O exposures at 80 K. No D$_2$ desorption was found when the D$_2$O coverage was smaller than ~ 0.23 ML. The low temperature D$_2$ peaks accompanying the desorption of D$_2$O originated from the
Figure 5.2a  Thermal desorption spectra (TDS) of D₂O predosed to different coverages. Curves 1, 2, 3, 4, 5, and 6 correspond to the 0 ML, 0.156 ML, 0.234 ML, 0.52 ML, 0.78 ML and 1.092 ML of coverage respectively. Peaks i, ii, iii and iv are located at 178 K, 163 K, 320 K and 336 K respectively. a) TDS of D₂O.
Figure 5.2b  Thermal desorption spectra (TDS) of D$_2$O predosed to different coverages. Curves 1, 2, 3, 4, 5, and 6 correspond to the 0 ML, 0.156 ML, 0.234 ML, 0.52 ML, 0.78 ML and 1.092 ML of coverage respectively. Peaks i, ii, iii and iv are located at 178 K, 163 K, 320 K and 336 K respectively. b) TDS of D$_2$. 
Figure 5.3  The integrated intensity of the thermal desorption peaks of: second D$_2$O adsorbed layer (filled squares), ice layer (filled circles) and D$_2$ (filled triangles) as a function of exposure. The top x-axis shows the coverage in monolayers (ML).
Figure 5.4 Schematic illustration of D$_2$O adsorption structure on Zr(0001) surface.
decomposition of $D_2O$ in the mass spectrometer. The $D_2$ peak centered above 300 K did not appear until coverages $> 0.23$ ML. It can been seen from Figure 5.3 that the intensities of the high T $D_2$ and the second layer peaks saturate at about the same exposure, indicating that the $D_2$ desorption occurring at $T > 300$ K originates from the second adsorbed layer of adsorbed $D_2O$. The implication is that the second adsorbed layer of $D_2O$ did not completely desorb as molecular water at 178 K, but that a small amount dissociated at a higher temperature, eventually yielding the desorption of molecular deuterium and leaving behind adsorbed oxygen in an undetermined chemical state.

5.1.3 Coverage resolved AES and SSIMS

Figure 5.5 shows the results of SSIMS measurement during adsorption at 80 K. The $OD^-$ uptake first follows a linear relation with coverage up to 0.23 ML, then increases at a slightly faster (but linear) rate up to a coverage of $\sim$ 0.6 ML, before gradually slowing. The first linear part corresponds to the adsorption of the chemisorbed layer for exposures resulting in coverages $\leq$ 0.23 ML. At higher exposures, the second adsorbed layer forms (chemisorption might still be occurring on uncovered areas of the surface). The increase in rate is probably due to a change in the SIMS yield of this ion which now arises from a molecular species. The decrease in the slope of ion yield versus coverage above $\sim$ 0.63 ML corresponds to the fact that the second layer becomes saturated and the ion yield is no longer affected by proximity to the metal surface as the adsorption of an additional water molecule changes only the thickness of the layer. A similar approach towards a constant yield can also be seen in $^{16}O^-$ and $^2H^-$ uptake curves.

Figure 5.6 shows the AES data under the same conditions as Figure 5.5, for the
Figure 5.5 SSIMS during D$_2$O exposure at 80 K. The adsorption can be divided into two linear uptake stages, 0 to 0.23 ML and 0.23 ML to 0.63 ML, followed by the formation of the ice layer.
Figure 5.6 The change of AES peak-to-peak height for the O(KLL), Zr(MNN), Zr(MNV)$_{me}$, Zr(MNV)$_{ox}$ transitions during the D$_2$O adsorption on Zr(0001) at 80 K.
O(KLL), the Zr(MNV) and Zr(MNN) transitions. The MNV transition is sensitive to the oxidation state of the Zr surface since the Zr(MNV) transition shifts from 147 to 140 eV when Zr$^9$ is oxidized to Zr$^{4+}$. The O(KLL) peak increased nearly linearly with $D_2O$ coverage up to \(~0.6\) ML. By comparing the O(KLL) differential peak-to-peak height to the absolute coverage determined by NRA at the same $D_2O$ exposure, the intensity of the O(KLL)/Zr(MNN) peak can be calibrated to the absolute amount of oxygen. Figure 5.7a illustrates the excellent linear relationship between the absolute coverage and the O(KLL)/Zr(MNN) ratio with a slope of 0.722. It can been seen from Figure 5.7b that the $D_2O$ uptake on Zr(0001) at 80 K follows a linear relationship: number of ML = 0.441 times the exposure in L. The Auger data for the MNV transition indicate the formation of oxide at coverage above \(~0.8\) ML. This is similar to the observations made in earlier studies of the reaction of Zr(0001) with $O_2$ [2].

Figure 5.8 shows the SSIMS data for a sample preexposed to $D_2O$ at 80 K to a coverage of 0.9 ML, and then heated. All 3 adsorbed species would be present: chemisorbed, second layer and ice layer. It can be seen that the $D_2O^-$ ion disappears above 200 K, the temperature by which all desorption of molecular water is completed. By contrast, the OD$^-$ ion yield decreased steadily at the very beginning of the heating, was then constant to \(~130\) K and decreased rather monotonically through the molecular desorption region, disappearing by \(~450\) K. It continued to decrease even in the region between \(~200\) and \(~270\) K in which no desorption was detected (Figure 5.2b). The disappearance of the OD$^-$ ion should be correlated with the infrared results which will be illustrated in Figure 5.10. While both data sets therefore support the idea that the OD
Figure 5.7  a) Comparison of the O(KLL)/Zr(MNN) ratio to the absolute coverage of oxygen determined by NRA;
b) Oxygen uptake kinetics during exposure of Zr(0001) to D₂O at 80 K, determined by calibration of the O(KLL)/Zr(MNN) ratio by NRA.
Figure 5.8  SSIMS on Zr(0001) with 0.9 ML D₂O preadsorbed at 80 K, as a function of temperature.
bond is being broken by reaction with the Zr surface, between \( \sim 250 \) and 350 K, the decrease in the OD\(^{-}\) SIMS yield below 250 K must also be partly attributable to loss of molecular water and possibly, changes in ion yields.

The O\(^{-}\) yield also first rapidly decreases and then stays constant to \( \sim 140\)-150 K and drops to a plateau after the completion of desorption of molecular water, before decreasing again at \( \sim 450\)-500 K, disappearing entirely by 800 K. The decrease in intensity below between \( \sim 140\) and 200 K is related to the desorption of the second adsorbed and ice D\(_2\)O layers. The origin of the initial rapid decrease is unknown but is most likely an artifact of the SIMS measurements as the experimental parameters stabilize. Figure 5.8b also illustrates the SSIMS yields for the ZrO\(^{-}\) and ZrO\(_2\)^{+} ions which decrease monotonically with temperature, the latter ion disappearing first (at lower temperature) as would be expected since the oxide will decompose first to produce dissolved O and a stoichiometry far from ZrO\(_2\).

5.2 Chemical states of absorbed D\(_2\)O

5.2.1 FTIR-RAS characterization of chemical states of adsorbed D\(_2\)O

Infrared reflection spectra for Zr(0001) exposed to D\(_2\)O at 80 K are illustrated in Figure 5.9. At the lowest coverages (below 90 s exposure, or < 0.52 L) when only the chemisorbed state is populated, a single absorbance feature is observed which is associated with an OD stretch at 2670 cm\(^{-1}\). There is no evidence for molecular water clusters which are characterized by a D-bonded band at 2543 cm\(^{-1}\) and a higher frequency peak which originates from non-H-bonded OD groups at the outside of the clusters. The absence of an
Figure 5.9  The FTIR-RAS spectra of Zr(0001) surface after different D$_2$O coverages. Curves 1, 2, 3, 4, 5, and 6 correspond to the 0.052 ML, 0.156 ML, 0.234 ML, 0.312 ML, 0.52 ML and 0.78 ML of coverage respectively. The absorption peak for the OD stretch in ice is at 2543 cm$^{-1}$; OD stretches are also visible at 2670 cm$^{-1}$ and 2732 cm$^{-1}$. 
IR signature for D\(_2\)O could originate from at least two causes. The first is that there is no molecular D\(_2\)O on Zr(0001) surface at low coverage (< 0.2 ML); the second is that the dipole of the adsorbed molecular D\(_2\)O is parallel to the Zr(0001) surface and that the surface selection rule is responsible for the absence of IR absorption. Our TDS data unequivocally point to dissociation of the water molecules at elevated temperatures, and the absence of any desorption for coverages below about 0.2 ML is circumstantial evidence for dissociation at still lower temperatures. Figure 5.10 illustrates the results of IR spectra taken to determine the nature of the OD species under conditions that dissociation is known to occur. The sample was exposed to about 0.35 L of D\(_2\)O at 80 K, warmed to the indicated temperature for a few seconds, and then recooled to 80 K, the IR absorption spectra then being acquired at 80 K. It is clear that the OD stretch does not shift in frequency, the implication being that dissociation must be occurring at the adsorption temperature of 80 K. The insert in Figure 5.10 shows the area of the OD absorbance peak as a function of the different annealing temperatures. The intensity of the OD stretch does not increase as the temperature is increased from 80 K, rather it decreases at T > 250 K, disappearing entirely by ~ 370 K. These data imply i) that all the D\(_2\)O adsorbed after 0.35 \(\ell\) exposure at 80 K, (~ 0.14 ML) dissociates upon adsorption and that the OD groups so formed are stable to T ≥ 250 K, and dissociate further between 250 and 350 K although no D\(_2\) desorption was detected because the D\(_{ad}\) diffuses into the bulk.

At higher exposures (coverages above ~ 0.3 ML; Figure 5.9) the expected hydrogen bonded OD stretch band is detected at 2543 cm\(^{-1}\) (corresponding to clusters of
Figure 5.10 The FTIR-RAS spectra of Zr(0001) surface after adsorption of 0.16 ML of D₂O at 80 K, followed by heating to indicated temperature, and cooling to 80 K. The insert shows the area of the OD absorbance peak remaining after the brief heating to the indicated temperatures.
D$_2$O) together with another peak at 2732 cm$^{-1}$ which is the non hydrogen-bonded OD stretch at the edge of molecular D$_2$O islands. The peak we have associated with adsorbed OD from dissociated water (which we will now term OD$_{ad}$), is still visible at 2670 cm$^{-1}$, although it is barely detectable in the spectrum at 0.78 ML and might be less intense by 0.52 ML. The correlation between the data in Figures 5.2a and 5.9 clearly indicate that the second adsorbed layer must consist mostly of molecular water. The coexistence of the OD$_{ad}$ from dissociated water and molecular water is interesting and suggests phase separation since the apparent decrease in the intensity from the OD$_{ad}$ species at high coverage might be due to D-bonding with molecular water, shifting its frequency into the 2543 cm$^{-1}$ band.

5.2.2 Work function change ($\Delta \phi$) during adsorption and desorption

Figure 5.11 shows the variation of $\Delta \phi$ of the Zr(0001) surface as a function of exposure (capillary array) to water at 80 K. $\Delta \phi$ was found to decrease with D$_2$O exposure, eventually saturating at $\sim$ 1.33 eV. The 0.23 ML of chemisorbed water is accompanied by a $\Delta \phi$ of -1.06 eV (80% of the total change). The work function continues to decrease with the formation of the second adsorbed layer, but is almost saturated by the point at which the second layer is completed.

Figure 5.12 illustrates the change in work function that occurs on heating the sample with 0.42 ML D$_2$O pre-adsorbed at 80 K (160 s capillary dosing). The work function starts to increase at $T \sim 190$ K, where the desorption of the second and ice layers is just completed. $\Delta \phi$ increases continuously up to 362 K, and then decreases to a minimum value at 593 K before then increasing again to a plateau at $T > 750$ K a
Figure 5.11 The change of work function ($\Delta \phi$) with D$_2$O exposure on Zr(0001) at 80 K. The absolute D$_2$O coverage at different exposures is also plotted. The label on the top of the graph indicates the adsorption stages defined by the thermal desorption experiments.
Figure 5.12  Work function change during heating for 0.42 ML of D$_2$O adsorption at 80 K. The heating rate is 1 K/sec for the solid line and 5 K/sec for the dashed line.
temperature at which all products of reaction should have dissolved or desorbed.

5.3 Structure of D$_2$O absorbed layer - LEED results

The Zr(0001) surface gave a sharp (1 x 1) hexagonal LEED pattern. No new fractional order pattern was formed upon adsorption of 0.25 ML of water, but the diffuse background intensity increased. However, if the sample was heated after water exposure, then a LEED pattern with apparent 2 x 2 symmetry could be produced, as shown sequentially in Figure 5.13. This pattern could arise from 2 domains of 2 x 2-O (each with less than the ideal coverage of 0.25 ML, but summing to 0.25 ML) spread between the first and second, and the second and third Zr planes. The intensity of this ordered LEED pattern increased with the D$_2$O coverage up to ~ 0.25 ML. At coverages above 0.25 ML, the fractional order spots elongate in the three symmetry directions rotated 120° to each other.

With the further increase of the D$_2$O exposure and coverage above 0.5 ML, a new LEED pattern emerges, shown in Figure 5.14. This is the LEED pattern of the Zr(0001) surface after dosing D$_2$O to a coverage of 0.6 ML, followed by annealing to 623 K for 30 seconds. In this case, no fractional order spots appeared until this annealing temperature is reached. The observed pattern appears to be a combination of (2 x 2) and (√3 x √3) patterns. Presumably this pattern could arise from coexistence of (2 x 2) and (√3 x √3) domains at coverages between 0.25 and 0.33 ML. Such a structure cannot be formed by oxygen exposure and annealing and again indicates kinetic control over the structures.
Figure 5.13  LEED pattern of Zr(0001) surface after annealing the sample at 450 K for 30 s.
   a) the clean surface;
   b) after 40 s D₂O adsorption at 80 K;
   c) after 120 s D₂O adsorption at 80 K;
   d) further annealing at 550 K for 30 seconds after c).
Figure 5.14  LEED pattern of Zr(0001) after 240 s D$_2$O exposure at 80 K followed by annealing at 623 K for 30 s.
5.4 Summary

The adsorption of $\text{D}_2\text{O}$ at 80 K can be divided into three stages: a chemisorbed layer (coverages between 0 and ~0.25 ML), second adsorbed layer, (up to a total coverage of ~0.65 ML) and an ice layer. The $\text{D}_2\text{O}$ in the chemisorbed layer is probably all dissociated into $\text{OD}_{\text{ad}}$ and $\text{D}_{\text{ad}}$, although we cannot eliminate the possibility of some further dissociation into $\text{O}_{\text{ad}}$ and $\text{D}_{\text{ad}}$. The second adsorbed layer is molecular water and begins to form before the chemisorbed layer is fully saturated. Molecular water can desorb from this layer at 173 K. The ice layer begins to form before the second adsorbed layer is fully covered, and desorbs with zero order kinetics at 163 K.

Adsorption of $\text{D}_2\text{O}$ at 80 K does not result in the formation of any new LEED superstructure. A (2 x 2) LEED pattern was observed upon annealing 0.25 to 0.5 ML coverages of adsorbed water above 450 K. The pattern probably originates from $\text{O}$ incorporated between the first and second Zr layers. A new $(\sqrt{3} \times \sqrt{3})$ LEED pattern was formed that coexisted with the 2 x 2 phase was formed at higher initial water coverages, followed by annealing above 600 K.
References


[3] see APPENDIX V
CHAPTER 6 CONCLUSIONS

The results of investigations on the interaction of $O_2$, $H_2(D_2)$ and $D_2O$ with Zr(0001) and Zr(10\bar{1}0) surfaces have been discussed in this thesis. The goal of these investigations was to provide the fundamental understanding of the factors that control the breakdown of the protective oxide barrier, hydrogen ingress and hydride formation in zirconium. The results are relevant to efforts to improve the quality, and eventually prolong the lifetime, of the zirconium alloy pressure tubes used in Candu nuclear reactor stations.

The diffusion coefficient of oxygen in zirconium at the operating temperature of the Candu nuclear reactor has been precisely determined by the experimental methods and theoretical model developed during the course of my work. The unique experimental method, which was realized by monitoring the dissolution of oxygen on a zirconium surface, made it possible to quickly determine (tens of minutes) the diffusion coefficient of an adsorbed species at a relatively low temperature. The experimental results were cross confirmed by measurements of the oxygen dissolution kinetics during both isothermal and continuous heating experiments. The diffusion coefficient was determined along two crystal directions, Zr(0001) ($D = 0.115\exp(-44.45\text{kcal/RT}) \text{ cm}^2/\text{s}$) and Zr(10\bar{1}0) ($D = 1.07\exp(-46.18\text{kcal/RT}) \text{ cm}^2/\text{s}$). By extending this method to measurements of the dissolution kinetics of the oxide film, we found that the oxide dissolution process controls the process of oxygen dissolution, rather than the oxide dissociation.

The hydrogen adsorption process was studied by NRA, SSIMS, AES, and $\Delta \phi$
measurements. It was found that the bond between hydrogen atoms and zirconium on the surface is energetically similar to that in zirconium hydride. Two types of adsorption site were characterized by work function measurements, one above the surface and another in the subsurface region. Since the lattice site is detectable by work function methods, it must lie within the screening length of the Zr valence electrons (< few tenths of nm). Hydrogen is slightly more tightly bound in the subsurface site than above the surface.

It was found that hydrogen has a very strong tendency to segregate to the surface of Zr. The segregant could form zirconium hydride as indicated by the features in the Auger electron spectra. The diffusion coefficients of hydrogen along the <0001> and the <10\bar{1}0> directions in a single Zr crystal were determined by the kinetics of surface segregation. It was found that the diffusion along <0001>, \( D = 3.40 \times 10^{-4}\exp(-9565/RT) \) cm²/s, is slower than that along <10\bar{1}0>, \( D = 1.73 \times 10^{-3}\exp(-8887/RT) \) cm²/s. This may be explained by the different atomic densities on the (0001) and (10\bar{1}0) faces, which affect the activation energy for diffusion.

The studies on the water adsorption are more complex than those of pure oxygen or hydrogen, not only because water is a molecule composed of oxygen and hydrogen, but interactions between these two species on the surface have to be considered. The adsorption of D₂O at 80 K can be divided into three stages: a chemisorbed layer (coverages between 0 and \( \sim 0.23 \) ML), second adsorbed layer, (up to a total coverage of \( \sim 0.65 \) ML) and an ice layer. The D₂O in the chemisorbed layer is probably all dissociated into OD\textsubscript{ad} and D\textsubscript{ad}, although we cannot eliminate the possibility of some further dissociation into O\textsubscript{ad} and D\textsubscript{ad}. The second adsorbed layer is molecular water and begins to
form before the chemisorbed layer is fully saturated. Molecular water can desorb from this
layer at 173 K. The ice layer begins to form before the second adsorbed layer is fully
covered, and desorbs with zero order kinetics at 163 K. Most of the water in the second
adsorbed layer desorbs molecularly at about 175 K, but some (~10 to 20%) dissociates
between 200 and 300 K to form either O$_{ad}$ and D$_{ad}$, or OD$_{ad}$ and D$_{ad}$ or a combination of
all three components. The OD$_{ad}$ species dissociate above ~240 K, and D$_2$ desorbs above
300 K. The observation of the desorption of D$_2$ is unusual, as with a “pure” D$_{ad}$ layer, all
the D dissolves into the bulk of the Zr sample. This could indicate that the O$_{ad}$ present
on/in the surface, prevents the dissolution of D. This mechanism is unlikely since we have
observed that adsorbed O actually reduces the barrier to dissolution of hydrogen.

Adsorption of D$_2$O at 80 K does not result in the formation of any new LEED
superstructure. A (2 x 2) LEED pattern was observed upon annealing 0.25 to 0.5 ML
coverages of adsorbed water above 450 K. The pattern probably originates from O
incorporated between the first and second Zr layers. A new (\(\sqrt{3} \times \sqrt{3}\)) LEED pattern that
coeexisted with the 2 x 2 phase was formed at higher initial water coverages, followed by
annealing above 600 K.
APPENDICES

The following appendices consist of copies (reprints and preprints) of the papers published during my PhD studies. Appendices I and II relate to the theory and its application for the determination of diffusion coefficients for oxygen diffusion in zirconium. Appendices III and IV show our theory on the explanation of the adsorption kinetics of hydrogen, and the segregation of the impurity hydrogen in zirconium. Appendix V details our investigation on the interactions of water with a zirconium surface.
APPENDIX I

Model and theory for the determination of diffusion coefficients by Auger electron spectroscopy measurements and an application to oxygen diffusion along the [0001] and [1010] axes in single crystal zirconium

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Abstract

A simple hopping model of the diffusion of adsorbed species from a surface into the bulk of a material has been formulated and solved mathematically. The difference in the energy barriers for an atom moving between the atomic layers at the surface and in the bulk are explicitly considered. This model is also capable of describing the initial stages of diffusion, something that conventional solutions of the continuum diffusion equation cannot handle. Auger electron spectroscopy has been used to measure the dissolution rate of oxygen from Zr(0001) and Zr(1010) surface into the bulk. Satisfactory results were obtained by applying our model to the diffusion data for these two zirconium surfaces for two different heating schedules: (i) rapid temperature ramp-and-hold and (ii) continuous linear heating with respect to time. The resulting Arrhenius expressions for diffusion are

\[ D = (0.115 \pm 0.031) \exp(-44.45 \pm 4.82) \text{ kcal/K cm}^2/\text{s} \text{ along Zr(0001)} \]

\[ D = (1.07 \pm 0.26) \exp(-46.18 \pm 4.22) \text{ kcal/K cm}^2/\text{s} \text{ along Zr(1010)} \]

Keywords: Auger electron spectroscopy, Diffusion and migration, Models of surface kinetics, Single crystal surfaces; Zirconium

1. Introduction

Diffusion is responsible for many phenomena in materials science and engineering such as segregation, grain growth etc. Diffusion has been extensively studied since the end of last century [1–4], and many techniques have been employed by scientists to determine the diffusion coefficients. Traditionally it is possible to measure the diffusion process directly through determination of a concentration profile of the diffusing element. First a composition profile is established by some process of deposition and annealing, the sample is then sectioned and the depth profile determined by analysis of the sections. With the development of modern surface analytical techniques, ion sputtering was introduced to section a sample, while secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to measure the composition at each stage in the depth profiling. The problem with this latter method is that the depth profile is modified by the experi-
ment through effects such as knock on, atomic mixing, sputter induced roughness and segregation that occur during sputtering. These effects are cumulative. Radioisotopes have been used to measure depth profiles in a nondestructive way, but the experiments are demanding and time-consuming. Also these methods can usually only measure the diffusion coefficient at relatively high temperatures where diffusion is rapid. Other methods of measuring volume diffusion coefficients at a quite low temperature, include ‘indirect’ methods such as internal friction and strain ageing. These methods are based on the theory that the movement of the impurity is the major factor responsible for strain relaxation. The explanation of the data is based on certain assumptions, but can yield the diffusion coefficient in a chosen crystallographic direction along which the solute atoms move to relax an applied strain [3,4].

The method which we employ here involves non-destructive analysis of the surface during diffusion. We report the development of experimental and theoretical methods and apply them to the study of the diffusion of oxygen in zirconium single crystals. This is an important technical system since zirconium alloys are used in the Canadian nuclear industry for in-reactor components such as pressure tubes (PTs). A zirconium oxide layer is grown on the pressure tube to protect against the ingress of hydrogen. The stability of this oxide film plays a crucial role in many materials applications. The dissolution of the oxide layer during operation at a temperature of 573 K [5] is one of the reasons for the breakdown of the oxide layer and the concomitant ingress of the hydrogen. Thus the kinetics of diffusion of oxygen in zirconium, especially at the reactor operating temperature, is an important parameter in the understanding of the stability of this zirconium oxide layer. Extensive efforts have been made to measure the diffusion coefficient of oxygen in zirconium; however, over the past 40 years. But, as noted by De González and García [6], many of the diffusion data in the literature were measured at high temperatures (> 873 K). Most of the data they reported were obtained from conventional techniques such as microhardness, strain aging, internal friction, etc. AES, SIMS or XPS depth profile techniques have also been introduced to determine the depth profile of the oxygen [7–12]. These methods are basically destructive, and the depth profile obtained is in fact a modified one, which will inevitably introduce errors as mentioned above.

Our group (Flinn, Zhang and Norton, FZN) [12], has used AES to dynamically monitor dissolution of oxygen adsorbed on the zirconium (0001) surface into the bulk. The advantages of this method are: (1) it can monitor the initial stages of the diffusion process and hence permits evaluation of the diffusion coefficient at rather low temperature; (2) it is a non-destructive method, and the surface is not physically or chemically modified during data acquisition as occurs in techniques such as SIMS; (3) it can determine the diffusion rate along a specific axis, the axis that is perpendicular to the surface. In our early report [12] we interpreted the data in terms of a simple model that assumed bulk-like diffusion behaviour through to the surface. The rate of disappearance of the oxygen on the surface is certainly connected to the diffusion rate of the oxygen inside the zirconium, but as we shall make clear below, the model was too simple. The diffusion behaviour along the c-axis obtained by using this method [12] was best fit by a model in which all the initially adsorbed oxygen was contained in a single crystal plane (so-called infinitely thin oxide layer (ITOL) model). However the value of D obtained by this analysis was one order of magnitude lower than that the accepted literature values [15], although it agreed with other values extrapolated from high temperatures. Recent measurements by Hood and co-workers [8] also suggested a higher value of D. The major errors in the analysis using the original ITOL model may arise from three sources: (1) the conventional diffusion equation cannot properly describe the initial stage of the diffusion process (this is actually the case, see Section 4); (2) diffusion has already occurred during heating the sample to a selected temperature in a temperature ramp-and-hold experiment, so the initial diffusion conditions are different from those for which the diffusion equation is derived; (3) the properties of the surface might be quite different from those of the bulk. For example, the surface may retain or reject solute elements due to effects of surface tension or differing surface adsorption potential wells. Other impurities segregated at the surface may also affect the dissolution rate of the adsorbed species. Furthermore, these species may
form a compound on the surface with quite different thermodynamic properties from the dissolved state. In the case of O on Zr(0001) our earlier studies in fact clearly demonstrated the presence of a (2 x 1) surface oxygen phase in which the oxygen atoms are believed to sit in octahedral holes between the first and second atomic Zr planes. This phase appeared to be more stable than the adsorbed state of O on this surface. There is therefore direct evidence of the occurrence of different behaviour at or near the surface. The appropriate mathematical model must therefore be used for analysis of the data. We have therefore set up a mathematical model to describe the diffusion process during the initial stages of diffusion, taking into consideration the possible differences between the energy barriers for atomic diffusion at the surface and in the bulk.

Based on these considerations, we have repeated the experiments described in Ref. [12] on Zr(0001), and have also applied them to a study of O diffusion from Zr(1010), the prism plane. The prism plane was studied since it is the same orientation as the surface orientation of the surface of the FTs. Diffusion along the direction normal to this plane should therefore be relevant to oxygen dissolution in the FTs. The experimental data obtained on the Zr(0001) surface were almost identical to the results of Ref. [12], while Zr(1010) shows slightly different behaviour. The new analysis of the data yields diffusion parameters in good agreement with literature values.

2. Experiment

The experiments were performed in a two-level ultrahigh vacuum chamber equipped with a Perkin-Elmer Physical Electronics single-pass cylindrical mirror analyzer (CMA) Auger spectrometer and the AES data were taken with a modulation voltage of 3 V. The chamber is pumped by trapped diffusion and Ti-sublimation pumps allowing base pressures of < 5 x 10^{-11} Torr to be achieved. As most of the information obtained by the AES originates from the surface and near-surface layers, the physical and chemical state of the surface is very important for the accuracy of the diffusion coefficient evaluated by our model. Zirconium is extremely reactive towards any residual gas present, especially H_2O, O_2, CO etc. which dissociate readily. In the current work the background pressure of water was below 10^{-11} Torr, and oxygen was undetectable. The filaments in the chamber were thoroughly out-gassed to ensure a very low CO background pressure (< 1 x 10^{-11} Torr) during the AES analysis.

The Zr (0001) and (1010) samples were cut from a 99.99% pure zirconium single crystal rod of 5 mm diameter provided by Chalk River Nuclear Laboratories of Atomic Energy of Canada Ltd. (AECL) and each sample was oriented and polished to within ± 0.5° of the 'nominal' (0001) or (1010) plane. The sample, supported by two platinum wires between copper posts, could be cooled to liquid-nitrogen temperature. A programmable temperature controller allowed for linear temperature ramps as well as isothermal experiments by resistive heating of the sample. The temperature was measured by a Ni-Cr/Ni-Al thermocouple spot welded on the edge of the sample. Heating rates of up to 70 K s^{-1} with virtually no overshoot (< 0.5 K) and temperature stability of < 0.5 K were routinely obtained.

The sample cleaning procedure was found to be quite simple, given a low base pressure (< 1 x 10^{-10} Torr), a low CO pressure (< 1 x 10^{-11} Torr) and clean argon sputtering gas. The sample, after being mounted in the UHV chamber, was first bombarded by 3 kV Ar^+ ions at a density about 3 μA cm^{-2} for 1 h to remove the original oxide layer and other contaminants (C, N, and F). During continuous sputtering, it was then heated to 1023 K for 30 min (to segregate the impurities to the surface region) and finally cooled to room temperature for another 30–45 min sputtering. This process produced an AES clean surface (C 1–2 at% and Cl, F, and O below the AES noise level, i.e. < 0.5 at%). The (0001) sample exhibited the expected (1 x 1) LEED pattern, but the clean (1010) LEED pattern was (1 x 4) [5]. Then the sample was exposed to 0.6 L oxygen (L = langmuir, 1 L = 1 x 10^{-6} Torr·s) at 90 K. We have previously shown that no zirconium oxide is formed at this exposure [5].

Two methods were applied to observe the diffusion of oxygen from the surface to the bulk. The first involved a series of experiments with identical and freshly prepared starting O-coverage, heating the sample very quickly (> 65 K/s) to a chosen temperature in 50 K increments in the range 473 to 773 K,
and monitoring the decrease of the O(KLL) AES intensity as a function of time at the final fixed temperature. The second method involved heating the sample linearly with respect to time at a slower rate (1 K/s) until the oxygen disappeared completely. The O(KLL) AES intensity was monitored during the process. The influence of the heating current on the AES signal was corrected by the calibration method described in Ref. [12].

3. Diffusion models

It was assumed in Ref. [12] that the disappearance of oxygen from the surface into the bulk of the zirconium crystal is controlled by the diffusion rate of the oxygen. This process was modeled by the solution to the diffusion equation for the dissolution of a thin film into a semi-infinite solid [1], i.e.,

\[ C(x, t) = \frac{M}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right), \]  

(1)

where \( D \) is the diffusion coefficient. \( M \) is the amount of the diffusing substance, \( t \) is the time, \( x \) is the depth from the surface and \( C(x, t) \) is the local concentration (molecules per unit volume) at \( x \) at time \( t \). This is the basis for the ITOL model which was described in Ref. [12]. In that particular experiment, the dissolution rate of a thin film was measured in a period of a few seconds. Thus we are dealing with the initial stage, or short time, behaviour of the diffusion process. It has been shown, see for example Ref. [13], that when transport is measured over sufficiently small times and distances the usual continuum description based on Fick’s law, as in the ITOL model, must be replaced by a discrete hopping model. This is thus an important factor in analyzing the experiments. The benefits of the extreme surface specificity of the in situ AES technique which provides the capability of very high depth resolution and sensitivity to low diffusion rates, also has as a consequence the possible drawback of the lack of local equilibrium in a typical measurement. Also, as mentioned in the introduction, a complete model should explicitly also consider the possible effects of the surface on diffusion kinetics.

In the discrete model we consider a semi-infinite solid in which the diffusing atoms migrate independently by nearest-neighbour hops between neighbouring atomic planes which are each parallel to the surface of the crystal. The concentration gradient is in the direction perpendicular to these planes and the concentration is thus laterally homogeneous, a situation easily realized experimentally. This one-dimensional model is characterized by the following quantities:

- \( a \) is the spacing of the neighbouring planes which are parallel to the surface,
- \( n \) is the distance of a plane from the surface plane in units of \( a \) (\( n = 0, 1, 2, . . . \)),
- \( c_n(t) \) is the concentration of the diffusing species at time \( t \) on the \( n \)th plane,
- \( w \), \( E \) are the jump frequency and the activation energy barrier, respectively, for an atom jumping to a nearest-neighbour site in the bulk (i.e. from planes \( n = 1, 2, 3, . . . \)),
- \( w_0 \), \( E_0 \) are the jump frequency and the activation energy barrier, respectively, for an atom jumping from the surface plane \( n = 0 \),
- \( z \) is the number of sites on plane \( (n+1) \) accessible by one jump from a site on plane \( n \).

The kinetic equations can now be written as

\[ \frac{\partial c_0}{\partial t} = -zw_0 c_0 + zwc_1, \]  

(2.1)

\[ \frac{\partial c_1}{\partial t} = -zw_0 c_1 + zw c_2 + zw_0 c_0, \]  

(2.2)

\[ \frac{\partial c_n}{\partial t} = zw(-2c_n + c_{n-1} + c_{n+1}). \]  

(2.3)

\( n > 2 \)

The jump frequencies \( w \) and \( w_0 \) may be written as

\[ w = A \exp(-E/kT), \]  

(3.1)

\[ w_0 = A_0 \exp(-E_0/kT). \]  

(3.2)

where the preexponential factors \( A \), \( A_0 \) and the activation energies \( E_1 \), \( E_0 \) are assumed independent of temperature. The bulk diffusion coefficient for this model is

\[ D = wza^2. \]  

(4)

By solving Eq. (2) (see Appendix A) with the boundary conditions

\[ c_0(0) = f, \]  

(5a)

\[ c_0(0) = 0, \]  

(5b)

\( n > 1 \).
we get
\[
\begin{align*}
c_s(t) &= \left[ I_\infty(\lambda t) - I_s(\lambda t) \right] e^{-bt} f \\
&\quad + W \int_0^1 ds \left[ I_0(t) - I(s) \right] e^{-ts} s \\
&\times \left[ (n+1) I_{n+1}(bs) - n I_n(bs) \right].
\end{align*}
\]
(5)

where
\[
\begin{align*}
c_s(t) &= f e^{-b} \left[ 1 - B b \int_0^1 ds \left[ I_0(bs) - I_s(bs) \right] \right] \\
&\times e^{-x \sin(\theta)} (W \neq 0),
\end{align*}
\]
(6)
\[
\begin{align*}
c_n(t) &= \left[ I_n(bt) + I_0(bt) \right] e^{-bt} f (W = 0).
\end{align*}
\]
(6.2)

and \( b = 2D/u^2 \), \( W = (w - w_0)/w \), \( \alpha = (1 - W)^2/2W \), \( \beta = (1 - W)/2W \). \( I_n(x) \) is the \( n \)th modified Bessel function.

It is obvious that \( W \) is a parameter by which we can evaluate the effect of the surface. When \( W = 0 \) (i.e., \( w = w_0 \)), the surface shows the same behaviour as the bulk, we have

\[
\begin{align*}
c_s(t) &= \left[ I_\infty(bt) + I_s(bt) \right] e^{-bt} f.
\end{align*}
\]
(7)

Our work uses AES to follow the time dependence of the decrease of the O(KLL) signal as oxygen atoms diffuse away from a Zr single crystal surface into the bulk. The intensity of electrons emitted decays exponentially with increasing depth with a characteristic inelastic mean free path (IMFP), which depends primarily on the electron energy. The intensity \( I(t) \) versus time thus can be calculated for the continuum description by integrating the concentration profile of the diffusing species with an exponential decay factor over all depths

\[
\begin{align*}
I(t) &= B \int_0^\infty C(x,t) \exp(-sx) dx
\end{align*}
\]
(8.1)

where \( B \) is a constant of proportionality, \( s = 1/\lambda \cos \alpha \), \( \lambda \) is the IMFP of the O(KLL) electrons (11.5 Å [14]) and \( \alpha \) is the electron collection angle measured with respect to the surface normal (42°). On the other hand, for the discrete model \( I(t) \) can be expressed in the form of summation

\[
\begin{align*}
I(t) &= B' \sum_{n=0}^\infty c_n(t) \exp(-sx_n) ,
\end{align*}
\]
(8.2)

where \( B' \) is a constant of proportionality and \( x_n = na \).

For the continuum description we substitute (1) into (8.1), and get the result of the ITOL model as in Ref. [12]

\[
\frac{I(t)}{I(0)} = \exp(y^2) [1 - erf(y)] ,
\]
(9)

where \( y = (Dt)^{1/2}/\lambda \cos \alpha \).

For the discrete model, we substitute (5) and (6) into (8.2) and get (see Appendix B):
(i) if \( W = 0 \)

\[
\begin{align*}
I &= f e^{-x} \left( 1 - b \beta \int_0^1 dy \left[ I_0(by) + I_s(by) \right] \right)
&\times e^{-x \sin(\theta)} (W \neq 0)
\end{align*}
\]
(6.2)

When \( t \) is large enough \( (bt \gg 1) \), this reduces to

\[
\begin{align*}
I(t) &= \frac{1}{1 - e^{-sx}} \frac{af}{\sqrt{\pi Dt}}
\end{align*}
\]
(10.2)

Here, and in subsequent equations, we omit the constant of proportionality \( B' \) for convenience.

(ii) if \( W \neq 0 \)

\[
\begin{align*}
I(t) &= f e^{-x} - \frac{f \beta}{\alpha - \alpha_1} \left( e^{x} - e^{x}\beta \right)
&+ \frac{f \beta}{\alpha - \alpha_1} \int_0^\infty dy \left[ I_0(by) + I_s(by) \right]
&\times e^{-x \sin(\theta)} \left( e^{x - x_1} - e^{x - x_1} \right),
\end{align*}
\]
(11.1)

and when \( t \) is large enough \( (bt \gg 1) \), this reduces to

\[
\begin{align*}
I(t) &= \frac{1}{1 - W e^{-x}} \frac{1}{1 - e^{-sx}} \frac{af}{\sqrt{\pi Dt}}
\end{align*}
\]
(11.2)

where

\[
\begin{align*}
\alpha_1 &= \frac{e^{x} + e^{-x} - 2}{2},
\end{align*}
\]
(12.1)

\[
\begin{align*}
\beta_1 &= \frac{W(e^{x_1} - 1) + (e^{x} - 1)}{2}.
\end{align*}
\]
(12.2)

The surface effect is represented by the parameter \( W \), which has the following physical properties:
(1) \( W < 0 \), i.e., \( w_0 > w \), \( E_0 < E \), the surface repels the solute atoms from the surface layer. These species accumulate at the layer beneath the surface and act
4. Results and discussion

The dissolution of oxygen from adsorbed layers on Zr(0001) and Zr(1010) at selected temperatures is shown in Fig. 2. It can be seen that dissolution is measurable at temperatures as low as 473 K, which means that we can in principle determine the diffusion coefficient at this temperature by the use of an appropriate model. The earlier work of FZM [12] found that the ITOL model described the dissolution behaviour better than other physical models of the initial O-structure, but the analysis was still based on continuum diffusion theory. The problem here is that the continuum diffusion theory itself cannot properly

as the limiting factor in the diffusion of these species into the bulk. The rate of decrease of the concentration of the solute is faster than for the situation in which there is no surface effect (i.e., \( W = 0, w_0 = \omega, E_0 = E \)).

(2) \( 1 > W > 0 \), i.e., \( w_0 < \omega, E_0 > E \), the surface has a tendency to hold the atoms. The surface concentration now decreases more slowly than for the case in which surface and bulk are identical. As the atoms are held at the surface, a depleted region is formed just beneath the surface. This is due to the atoms just beneath the surface jumping back to the surface. A consequence of some importance for this situation is that if the initial sample condition has the solute distributed homogeneously throughout the bulk, solute segregation at the surface can occur.

(3) \( W = 0 \), i.e., \( w_0 = \omega, E_0 = E \), the surface shows the same behaviour as the bulk.

(4) \( W = 1 \), i.e., \( w_0 = 0, E_0 = \infty \), the surface becomes a sink to hold the atoms and a surface compound may be formed.

Fig. 1 illustrates how the surface parameter \( W \) affects the dissolution process. The rate of change of the concentration of the surface species (AES intensity) calculated from Eqs. (10) and (11) is clearly dependent on this parameter in the expected manner.

![Graph showing the variation in dissolution rate of surface species due to different surface energy barriers. The curves are computed from Eqs. (10) and (11).](image1)

![Graph showing the dissolution of oxygen from adsorbed layers on Zr(0001) and Zr(1010) at selected temperatures. The dissolution is measurable at temperatures as low as 473 K.](image2)
describe the dissolution process under our experimental conditions. The discrete diffusion theory is more accurate than the continuum diffusion theory for dealing with the problem of 'short time' data. For long times (bt > 1), the discrete diffusion theory (Eq. (7)) reduces to the results of continuum diffusion theory (Eq. (1)).

Fig. 3 shows the comparison of the ITOL model and the model based on the discrete method (Eq. (10.1)) (at this stage we have not included the effect of different surface potential wells). It can be seen that the two models show a significant difference at bt < 10^3, with the diffusion process predicted by the discrete model being slower than that predicted by the continuum model. This is because the continuum model overestimates the driving force for diffusion at this stage. It is therefore not surprising that the discrete model will yield larger diffusion coefficients than the continuum model if they are both used to fit to the same set of data.

For oxygen diffusion in zirconium, the diffusion coefficient is between 10^{-21} and 10^{-15} cm^2/s at 473 to 673 K [15]. The interlayer spacing in zirconium is of the order of 10^{-4} cm. Then b = 2D/a^2 = 10^{-5} to 10 s^{-1} for this case. In our experiment, the measurement time is from t = 0 to 100 s, and therefore bt = 10^{-3} to 1000. This is in the range of 'short time' behaviour (Fig. 3) and confirms that our data must be described by the discrete diffusion theory.

The first step in applying our model is simply to assume that the surface and bulk behaviours are identical (W = 0). We then employ Eq. (10.1) to fit our data and obtain the results plotted as closed circles and triangles in Fig. 4. We can see that analysis using the discrete model gives values of D about one or two orders of magnitude higher than those from the ITOL model, and about half an order of magnitude higher than the results in the literature [15]. Furthermore, we see that the diffusion rate along two axial directions normal to the surface of the two zirconium single crystal samples, [0001] and [1010], is almost the same. The vertical dotted line indicated on the graph is at 573 K, which shows that our method can readily extend determination of the diffusion data to temperatures appropriate to operation of nuclear reactors.

We now take into consideration the possible effects of different surface potential wells by explicitly calculating the effect of the difference in energies for an atom leaving the surface (E_n) and that for a solute atom moving inside the bulk (E). In order to find the proper W value, polynomial fits for K(t) against bt were determined for a series of different W values through Eq. (11.1). The experimental data are then fitted to these polynomial expressions and a series of diffusion coefficient D are found for these W.
The fitting error \( \text{Err} \), the square root of the sum of squares of the residuals, is also determined in each case. Fig. 5 is a typical plot for the change of \( D \) and \( \text{Err} \) for different values of \( W \). We can see from Fig. 5 that the best fit is obtained within a range of \( W \) (± 0.5), therefore the \( D \) we obtain does not have a single, unique value but is reliably determined within some error limits in a certain range. Fig. 5 shows that \( D \) does not change too much within this range of \( W \) (\( D \) is quite sensitive to \( W \) when \( W \) approaches one). The results of this fitting procedure are plotted as the open data points in Fig. 4; these are the mean \( D \) of our fitting at each temperature and are also listed in Table 1. The error bars on the open data points indicate the range of \( D \) values that best fit the experimental data using the procedure just described. The diffusion coefficients so derived are smaller than those obtained without allowance for the effect of the surface potential well, and closer to the literature values [15]. The result of including the surface effect is larger for diffusion normal to the (0001) surface than for the (10\( \bar{1} \)0) surface. The relationship of \( W \) to temperature, \( T \), is shown in Fig. 6. We can see from Table 1 that \( W \) is negative and in the range -1.4 to -0.4. This means that the surface tends to push the oxygen away from the surface, the oxygen accumulating in the atomic layer just under the surface. The calculated surface effect is relatively small as \( W \) is negative and not very large. The resulting Arrhenius expressions for the diffusion coefficient of oxygen now are:

\[
2^{13^1} = (0.115 \pm 0.031) \times \exp\left[\frac{-44.45 \pm 4.82}{RT}\right] \text{cm}^2/\text{s},
\]

for \( \text{Zr}(0001) \), (13.1)

\[
D^{13^2} = (1.07 \pm 0.26) \times \exp\left[\frac{-46.18 \pm 4.22}{RT}\right] \text{cm}^2/\text{s},
\]

for \( \text{Zr}(10\bar{1}0) \). (13.2)

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( D^* ) (m(^2/\text{s}))</th>
<th>( D ) (m(^2/\text{s}))</th>
<th>( W )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0001)</td>
<td>(10( \bar{1} )0)</td>
<td>(0001)</td>
</tr>
<tr>
<td>523</td>
<td>5.129 \times 10^{-18}</td>
<td>2.512 \times 10^{-18}</td>
<td>3.214 \times 10^{-26}</td>
</tr>
<tr>
<td>573</td>
<td>9.323 \times 10^{-18}</td>
<td>4.890 \times 10^{-18}</td>
<td>9.322 \times 10^{-26}</td>
</tr>
<tr>
<td>623</td>
<td>2.766 \times 10^{-18}</td>
<td>1.844 \times 10^{-18}</td>
<td>4.411 \times 10^{-26}</td>
</tr>
<tr>
<td>673</td>
<td>-</td>
<td>1.018 \times 10^{-16}</td>
<td>-</td>
</tr>
<tr>
<td>723</td>
<td>1.949 \times 10^{-14}</td>
<td>1.457 \times 10^{-13}</td>
<td>3.084 \times 10^{-26}</td>
</tr>
<tr>
<td>773</td>
<td>-</td>
<td>1.227 \times 10^{-13}</td>
<td>-</td>
</tr>
</tbody>
</table>
Here we use the superscripts 1 and 2 to indicate the (0001) and (10\bar{1}0) surfaces, respectively. The energy barrier at the surface can also be calculated by the equation

\[ E_u = E - RT \ln(1 - W) \]  

where we ignore any possible differences in the pre-exponential factors \( A, A_0 \) in Eq (3).

The value of \((E_u - E)/R\) can be obtained from the slope of the line of \(\ln(1 - W)\) versus \(T^{-1}\) shown in Fig. 6, where we ignore any possible difference in pre-exponential in (3.1) and (3.2). We obtain surface energy barriers of \(E_u^{1/2} = 43.54\) kcal, \(E_u^{1/2} = 45.65\) kcal, which are 97.97% and 98.87% of the energy barrier for an atom moving inside the bulk. The effect of the surface is not strong in this system.

The second method used to observe diffusion of the oxygen, is to heat the sample continuously and linearly with respect to time, to a high temperature while monitoring the dissolution rate of the oxygen with AES. This continuous heating method eliminates the errors which result from the ramp-and-hold heating method, such as the temperature overshoot and oxygen loss during the heating process [16]. Moreover, it is much easier to implement experimentally. The diffusion coefficient relation can be determined just from a single heating run. Fig. 7 shows the decrease of the surface oxygen concentration as the temperature is increased. In order to interpret this experiment some modifications of the earlier model analysis must be made.

We first define

\[ \bar{w} = \frac{1}{t} \int_0^t w(t') \, dt' \]  

and employ \(\bar{w}t\) in place of \(t\) as the variable in the kinetic equation. When the surface effect is neglected, i.e., \(w = w_0\), Eqs. (2) become

\[ \frac{\partial c_0}{\partial (\bar{w}t)} = -c_0 + c_1, \]  

\[ \frac{\partial c_2}{\partial (\bar{w}t)} = -2c_a + c_{a-1} + c_{a+1}. \]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.png}
\caption{AES data for dissolution of oxygen during a linear temperature ramp}
\end{figure}
These equations can be solved by the procedure used for solving Eqs. (2). In this way we obtain a similar result to Eq. (10) for the intensity:

\[ I(t) = \int e^{i \mathbf{k} \cdot \mathbf{r}} \left[ 1 - 2\mathbf{b} \cdot \mathbf{r} \right] \mathbf{d} \mathbf{r} \left[ I_0(\mathbf{b}) + I_1(\mathbf{b}) \right] \times e^{-i\gamma^2 \mathbf{r} \cdot \mathbf{a}^2} \]

\[ = 2 \sum \left( -2 \mathbf{b} \cdot \mathbf{a}^2 \right) \]  

\[ = 2 \mathbf{b}^2 - 2 \mathbf{b} \mathbf{a}^2 \]  

This allows one to calculate \( I(t) \) for a given value of \( \mathbf{b} \) and so construct a polynomial fit for \( \mathbf{b} \) as a function of \( I(t) \):

\[ \mathbf{b} = \sum \left( \begin{array}{c} a_2 \end{array} \right) I^2(t). \]  

The agreement between the two experiments and the two methods of analysis provides confidence about our diffusion data and the calculations. Diffusion along two crystal directions normal to (0001) and (1010) planes is very similar. We know that oxygen occupies the octahedral interstitial sites in bcc zirconium crystal (Fig. 9). For oxygen moving along (0001), i.e. from position 1 to position 2 in Fig. 9, the oxygen atom has to go through the close-packed plane (0001). One might expect that the energy barrier to this diffusion process should therefore be

\[ D(T) = \frac{a \gamma^2}{2} \sum_{k=1}^{n} \frac{a_2 I^2(t)}{dI/dT}. \]  

The relationship between \( I \) and \( T \) and between \( dI/dT \) and \( T \) can be determined from experimental results, Fig. 7. An Arrhenius plot of the diffusion coefficients determined in this way is compared with the results from the ramp-and-hold experiments in Fig. 8. The analyses of both types of experiment neglect any possible surface effect (\( \gamma = \gamma_s \)). It is clear that the result from the analysis of the continuous heating data is quite consistent with the data obtained from the ramp-and-hold experiments without inclusion of the surface effect. The inclusion of the surface effect results in a reduction in the calculated values of the diffusion coefficients.
larger than for atomic motion through other, more open planes. For oxygen moving along [10\overline{1}0], i.e., from position 1 to 3, the oxygen atom could jump to tetrahedral sites, position 4, first and then move to its destination site 3. Simple bond counting arguments indicate that similar numbers of bonds are broken along the two paths, so perhaps the similarity of activation energies can be explained rationally in that manner.

Our model gives a consistent interpretation of the experimental data. We caution that this model ignores the possible effects of saturation and lateral interaction between the adsorbed species. Care should be exercised when applying this model to a system where the surface coverage is high and the surface effect is very strong (\( W \) approaches 1). As we mentioned above, oxygen forms a relatively stable surface phase on zirconium, (2 \times 1) on (0001) and (2 \times 4) on (10\overline{1}0); the stable position for oxygens in the (2 \times 1) phase on Zr(0001) is in the octahedral interstitial sites between the topmost and second atomic planes. These observations suggest that the W should be positive rather than the negative value we obtained. This might indicate that the surface effect on adsorbed species is not just limited to the top layer, as assumed in our simplified model. There might therefore be a depleted region under the stable phase. The analysis of these results is currently beyond the ability of our experimental techniques.

5. Conclusion

We have developed experimental methods and an appropriate discrete mathematical model to permit the determination of the diffusion coefficient of oxygen in zirconium at rather low temperatures. The method itself is not just limited to this specific system and has the potential to be applied to other systems [5,14]. We found that the zirconium surface has a strong effect on the dissolution of the oxygen in the temperature range 473 to 673 K. The diffusion rates of oxygen along two different crystal directions in zirconium, i.e., normal to the (0001) and (10\overline{1}0) surfaces, are very similar. The present model provides a good description of our experimental data although a complete model should also include the effects of saturation and lateral interaction [17].

Acknowledgements

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Appendix A. Derivation of \( c_m(t) \)

In this Appendix we give the details of the derivation of Eqs. (5) and (6) for the diffusant concentrations. It is derived as a result of using a model with greater symmetry. We therefore consider a system of \( 2N + 2 \) atomic planes at right angles to the \( x \)-axis and with periodic boundary conditions. The planes are labelled from the left by \( m = 1, 2, \ldots, 2N + 2 \). For jumps from planes \( N + 1 \) and \( N + 2 \) the jump frequency is \( \omega \), and for jumps from all other planes the jump frequency is \( \nu \). The initial condition for the concentration \( c_m(t) \) at plane \( m \) is

\[
c_m(0) = f, \quad m = N + 1, N + 2.
\]

\[
c_m(0) = 0, \quad m = N + 1, N + 2. \tag{A.1}
\]

Since the jumps between the adjacent planes \( N + 1 \) and \( N + 2 \) occur with equal frequency in either direction the changes in concentrations in the two half planes, extending from \( n = 1 \) to \( N + 1 \) and from \( N + 2 \) to \( 2N + 2 \), will both be the same as if each were isolated from the other. Thus the solution for either half plane will furnish the solution of the discrete model defined in Section 3, after appropriate relabelling of the sites.

The kinetic equation for the model is

\[
\frac{d c_m}{dt} = 2\nu(-2c_m + c_{m-1} + c_{m+1})
\]

\[
+ \nu(w_0 - w)[\delta_{m,N+1}(c_{m-1} - 2c_{m-1} + c_{m+1})
\]

\[
+ \delta_{m,N+2}(-2c_{m+1} + c_{m+1})
\]

\[
- (\delta_{m,N+1} + \delta_{m,N+2}c_{m+1}). \tag{A.2}
\]
The solution is most simply obtained using the discrete Fourier transform,
\[
c(k) = \sum_{m=0}^{2n-2} e^{-ikx_m} c(x_m),
\]
where \(x_m = a(m - 1)\) is the position of the \(m\)th plane and \(a\) the spacing between neighbouring planes. The Fourier transformed equation can be integrated with respect to time to obtain
\[
c(k) = G(k, t) c(k, 0) + b W y(k) \int_{0}^{t} ds \ G(k, s) \left[ e^{-ikv_{s+1}c} (t-s) + e^{-ikv_{s-1}c} (t-s) \right].
\]
where
\[
G(k, t) = e^{-b t |k|},
\]
and, as in the main text, \(b = 2 \pi w\) and \(W = (w - w_o)/w\). The initial value appearing in the equation for \(c(k, t)\) is found from (A.11) and (A.3) to be
\[
c(k, 0) = (e^{-ikv_{s+1}c} + e^{-ikv_{s-1}c}) f.
\]

The Fourier transform in (A.4) is next inverted using the identity
\[
c_m(t) = \frac{a}{2 \pi} \int_{-\pi/a}^{\pi/a} dk \ e^{-ikx_m} c(k, t).
\]

The results will be the sum of a contribution which we denote \(c_{m}^{0}(t)\), arising from the first term on the right of Eq. (A.4), which is independent of \(W\) and a term denoted \(c_{m}^{1}(t)\) which depends on \(W\):
\[
c_m(t) = c_m^0(t) + c_m^1(t).
\]

It is sufficient to focus attention on the right half plane by putting \(m = (N-1) + n\) so that \(n = 0, 1, 2, \ldots\) labels the right half plane with \(n = 0\) being the plane in which the jump frequency is \(w_o\). With this labelling the solution for this half plane will be the same as for the model in the main text. For the term independent of \(W\) we obtain
\[
c_m^{0}(t) = \left( \frac{1}{2 \pi} \int_{-\pi/a}^{\pi/a} dk \ \left[ e^{-ikx_{m+1}c} + e^{-ikx_{m-1}c} \right] e^{-b t f} \right.
\]
\[
\times e^{- \pi b \int_{0}^{t} ds \ \left[ I_{s+1} (bs) + I_{s-1} (bs) \right]} \left. e^{-b t f} \right).
\]

When the two exponentials containing \(n\) are expanded according to the identity \(\exp(x) = \cos(x) + i \sin(x)\), one obtains
\[
c_m^{0}(t) = \left[ I_{m+1} (bs) + I_{m-1} (bs) \right] e^{-b t f} \quad (A.11)
\]

For the term dependent on \(W\) we obtain in a similar way, after minor manipulation,
\[
c_m^{1}(t) = \frac{b W}{2} \int_{0}^{t} ds \ \left[ I_{m+1} (bs) - I_{m-1} (bs) \right] \left[ I_{m+1} (bs) - I_{m-1} (bs) \right]
\]
\[
+ W \int_{0}^{t} ds \ c_m(t-s) \frac{e^{-b t f}}{s}
\]
\[
\times \left[ (n + 1) I_{n+1} (bs) - n I_{n} (bs) \right].
\]

Eqs. (A.9), (A.10) and (A.11) combine to give Eq. (5) of the main text.

In order to complete the solution we must determine an explicit expression for \(c_n(t)\) from Eq. (5) with \(n = 0\):
\[
c_0(t) = \left[ I_{1} (bt) + I_{0} (t) \right] e^{-b t f} \quad + W \int_{0}^{t} ds \ c_0(t-s) \frac{e^{-b t f}}{s}
\]
\[
\times \left( (1 - W) \frac{\sqrt{p + 2 b - \sqrt{p}} - W}{\sqrt{p}} \right)
\]
\[
\times \left( \sqrt{p} \right)
\]
\[
\times \left( -b \frac{\sqrt{p + 2 b - \sqrt{p}} + W}{\sqrt{p}} \right)
\]
\[
\times \left( \frac{f}{p - a b} \right).
\]

When \(W \neq 0\) we may divide top and bottom of the fraction in the second brackets and write
\[
c_0(t) = \left( -b \frac{\sqrt{p + 2 b - \sqrt{p}} + W}{\sqrt{p}} \right)
\]
\[
\times \left( \frac{f}{p - a b} \right).
\]

where \(\alpha = (1 - W) / 2 W, \beta = (1 - W) / 2 W\). The inverse of this equation is
\[
c_0(t) = \int_{0}^{t} ds \ e^{-b t f} \left[ I_{1} (bs) + I_{1} (bs) \right]
\]
\[
\times e^{- \pi b \int_{0}^{t} ds \ \left[ I_{s+1} (bs) + I_{s-1} (bs) \right]}
\]

\[
(A.17)
\]
Appendix B. Derivation of $I(t)$

In this Appendix we outline the derivation of Eqs. (10) and (11) for the intensity. The expression for the intensity in the discrete model, Eq. (8.2), is first differentiated with respect to time and the kinetic equations (2.1)–(2.3) then employed to eliminate each $dc_n/dt$ ($n = 0, 1, 2, \ldots$) in terms of products of jump frequencies and concentrations. When Eq. (8.2) is employed to eliminate all the summations of $c_n \exp(-\alpha sc_n)$ in terms of intensity the result is

$$\frac{dI(t)}{dt} = \alpha_1 b l(t) - \beta, \quad (B.1)$$

where $\alpha_1$ and $\beta_i$ are defined in Eq. (12) in terms of $sa$ and $W$. Here, as in Section 3, we have taken the constant $B'$ in the definition of $l(t)$, Eq. (8.2), to be unity.

Eq. (B.1) can be Laplace transformed with respect to time and then solved for the transform, $I(p)$, of the intensity. By employing the initial value, $I(t = 0) = f$, one obtains

$$l = \frac{f}{p - \alpha_1 b} - \frac{\beta_i b}{p - \alpha_1 b} c_0. \quad (B.2)$$

When the expression for $c_i(p)$ in Eq. (A.16) is substituted into this expression and the Laplace transform is inverted one obtains Eqs. (10.1) and (11.1) for the intensity $I(t)$.

References

Appendix II

The reconstructed clean Zr(1010) surface and its interaction with oxygen

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Abstract

The preparation and reactivity of the Zr prism plane, Zr(1010), have been studied by LEED, NRA, AES and work function methods. The clean (1 x 1) surface, prepared by sputtering, is metastable, reconstructing to a (1 x 4) phase above ~773 K. This (1 x 4) surface is stable upon cooling to low temperature. Oxygen adsorption has been studied on this surface at 90, 293 and 373 K. At the higher temperatures, oxygen absorbs into subsurface sites, forming a (2 x 4) superlattice at a coverage of ~8 x 10^14 O cm^-2. Oxide is then formed, growing layer-by-layer at 90 K to a thickness of ~12 Å. Oxide dissolution was studied by measurements of the change in the oxide thickness at a series of temperatures for a constant initial coverage prepared at a fixed and low temperature. The rate-controlling step in oxide dissolution is O diffusion into bulk Zr.

1. Introduction

Zirconium and its alloys are widely used in the nuclear industry for a number of reasons, including low neutron absorption and excellent corrosion resistance to water at 300°C [1]. The Zr-Nb alloys used in the Candu (Canada Deuterium Uranium) reactor afford improved creep resistance and strength. At high temperatures, hydrogen isotopes, either deliberately added or present as a result of radiolysis or corrosion reactions, may diffuse into the bulk of components fabricated from Zr. A thin oxide film formed on the surface by oxidation of zirconium in air or water is designed to prevent hydrogen ingress. The autoclaving treatment given to pressure tubes following fabrication for stress relieving purposes increases the thickness of this protective oxide film. Extensive effort has been devoted to studies of the oxidation of Zr, including studies on the initial stages of oxidation of single and/or polycrystalline Zr samples by using surface analytical techniques [2-24]. However, the studies on single-crystal Zr have been restricted to the Zr(0001) surface. In a practical sense, understanding the oxidation behavior of the prism plane, Zr(1010), is even more important than that of the basal plane, Zr(001). After cold rolling, the grains in a Zr alloy pressure tube are usually oriented such that the surface of the component is mainly composed of Zr(1010) planes. Therefore, the oxidation of these Zr components is actually occurring on the Zr(1010) surface. To date, there have been no studies on the oxidation of the prism plane.
Zr(10\bar{1}0). It is of interest to investigate the atomic arrangement of this more open surface when clean, as well as the structural and kinetic phenomena involved in its interaction with simple gases. In this paper, we report on the observation of reconstruction of the clean Zr(10\bar{1}0) surface as well as results on its reaction with oxygen. We will compare the present results with those on the oxidation of the basal plane, Zr(0001) which has also been investigated in this laboratory [2-5].

It is known that the oxide film on Zr dissolves into the bulk at high temperature and this process can occur on Zr and Zr-alloy nuclear components at common reactor operating temperatures (for example 300°C in a Candu reactor). In order to reduce the rate of oxide dissolution and, thus, retain a high quality oxide film on the surface of Zr components, a full understanding of the dissolution process, including controlling factors such as kinetics etc. is crucial. In the present study of Zr(10\bar{1}0), the emphasis is on factors controlling dissolution of the oxide film.

2. Experimental

The experiments were performed in a two-level ultrahigh vacuum chamber equipped with low energy electron diffraction (LEED), secondary ion mass spectrometry (SIMS; with Ar+ and Cs+ beam facilities), thermal desorption spectroscopy (TDS), and a Kelvin probe for work function measurements (\Delta \phi) on the upper level, and Auger electron spectroscopy (AES; with profiling capability) and nuclear reaction analysis (NRA) on the lower level. The base pressure in the chamber, lower than 3 \times 10^{-11} Torr, was achieved by employing a trapped diffusion pump and a Ti sublimation pump. The chamber is interfaced to a 2.5 MeV Van de Graaff accelerator via two stages of differential pumping as described elsewhere [2].

The LEED experiment was carried out by using a video-LEED system. The LEED pictures were digitized by a computer from the video tape and analyzed later. The angle of incidence was close to 90°.

The Auger signals were measured by employing a computer-controlled single-pass cylindrical mirror analyzer (CMA) spectrometer. The beam energy and current were 3 keV and 0.2 \mu A, respectively. The electron beam was rastered over a 0.2 mm × 0.2 mm area, which yielded a current density of 5 \mu A/mm². No visible damage was found on the oxide-covered sample under bombardment by this electron beam. A modulating voltage of 1 V and a scanning rate of 30 eV/s were used in the AES experiments. The fast scanning rate was chosen to permit collection of sufficient data in the isothermal experiment at higher temperatures, where the Auger signals changed rapidly. During heating, the magnetic field produced by the heating current which passes directly through the sample affects the Auger signals. The correction for this effect was made by performing a "blind" AES experiment in which various Auger signals were monitored during heating and in which the surface composition did not change. A suitable stable surface was produced by a saturation exposure to oxygen at 90 K, the Auger intensities then being measured during heating to 300 K. The correction factors due to the heating current on the various Auger signals were obtained from this experiment. These correction factors were then applied to the AES data from isothermal experiments in which the heating current was also recorded.

The characteristics and parameters used in NRA (nuclear reaction analysis) and \Delta \phi (work function measurement) experiments have been described earlier [3]. The accuracy of the absolute oxygen coverage measured by NRA is about 3–5%. The RMS noise level for a \Delta \phi measurement is \sim 1 mV at a response speed of \sim 100 ms.

The sample was cut from a 99.99% pure zirconium single-crystal rod of 5 mm diameter provided by Chalk River Laboratories of AECL and oriented and polished to within \pm 0.5° of the prism plane. It was found that impurity Fe has a very strong tendency to segregate to the surface even at bulk concentrations as low as tens of ppm [4]. For a freshly cut and polished sample, after removal of the surface impurities such as adsorbed C and O, the surface composition of Fe can reach tens of atomic percent after annealing at high temperature. In order to produce a sur-
Fig. 1. Typical Auger spectrum of the Zr surface after cleaning. Fe is detectable at a level estimated to be ~1.3%. No additional segregation occurs at any annealing temperature.

face as free of Fe as possible for the present measurements, it was essential to produce a sample from which all segregable iron had been removed. The removal of bulk impurity Fe was achieved by annealing the sample at 873 K with simultaneous and extensive Ar⁺ sputtering until all no-Fe segregation could be detected after the regular sputter and anneal cleaning procedure [2]. The surface concentration of Fe could be reduced to a level close to the detection limits of Auger spectroscopy (~ 1-2%) after this process. Fig. 1 illustrates a typical Auger spectrum of a clean surface and shows the barely detectable Fe signal and very small signals of C and O. Consideration of cross sections indicate a total surface contamination of ~ 2%. We never observed any influence of these contaminants on the results reported below.

3. Results and discussions

3.1 Reconstruction of the clean Zr(1010) surface

LEED data obtained after sputtering at 90 K with a current density of 20 μA/cm² Ar⁺ for 30 min showed a uniform bright background indicating considerable disorder of the surface region. After heating this sputtered sample to room temperature, a very weak and diffuse LEED (1 × 1) pattern emerged, indicating that some annealing has occurred. With increasing sample temperature, the (1 × 1) LEED pattern intensified and the integral order diffraction beams sharpened (Fig. 2a) until the sample temperature reached ~773 K at which temperature fractional order spots appeared, forming a (1 × 4) LEED pattern (Fig. 2b). The (1 × 4) nomenclature indicates that the surface superstructure has a periodicity parallel to the (0001) bulk direction which is four times longer than in the bulk. With increasing sample temperature up to just below the phase transition temperature of 1136 K, the (1 × 4) pattern becomes sharper. The (1 × 4) superstructure was

![Image](https://example.com/image1)

![Image](https://example.com/image2)
stable upon cool-down to 90 K and to all subsequent thermal cycling in the range 90 < T < 1100 K. No impurities were detected on the surface (above the background ~1% level) when the superstructure was formed. This fact combined with the high intensity of the fractional order beams indicates that the (1 x 4) pattern arises from a reconstruction of the Zr surface and that the (1 x 1) phase is metastable. Many metal surfaces, particularly those having a low atomic density (such as fcc (110), bcc (100), etc.), are known to reconstruct [25], but to our knowledge, the reconstruction of Zr(1010), or of (1010) surface of any hcp metal, has never been reported in the literature.

The superlattices formed on clean surfaces are often very sensitive to small coverages of contaminants, such as H, O, CO etc., reverting to the unreconstructed (1 x 1) phase [25]. This is not the case for the Zr(1010)-(1 x 4) surface. Low coverages of oxygen adsorbed on the Zr(1010)-(1 x 4) surface did not change the (1 x 4) superlattice to the (1 x 1) structure (see below). Hydrogen exposures up to 1 L caused no change in the (1 x 4) symmetry but did cause an increase in the background intensity and a reduction of the intensities of the LEED beams. Surprisingly, Fe segregation at levels up to several at% appeared to have no influence upon the formation of the (1 x 4) phase. This raises the question as to whether the reconstruction is connected with impurity segregation. However, the (1 x 1) to (1 x 4) transition also occurred at T = 773 K for all Fe segregation levels down to the lowest achievable of ~1%. Therefore, we believe that the reconstruction is an inherent property of the clean (1010) surface.

3.2. Initial oxidation

Oxygen interaction was only studied on the stable reconstructed (1 x 4) surface. Fig. 3 shows the uptake of oxygen on Zr(1010)-(1 x 4) surface measured by NRA at 90, 293 and 473 K, respectively. The origin of the sequence of reactivities at > 5 langmuirs (1 L = 1 x 10^{-6} Torr s) has been discussed in detail for the case of oxidation of Zr(0001) [3]. It appears that similar discussion is appropriate for the present system. The initial sticking coefficient, S, is 1 at low coverage at all three temperatures. At 90 K, S remains high to very high coverages. At 293 K the rate of oxidation falls rapidly for exposures above ~ 5 L, while remaining a little higher at 473 K. The origin of the enhanced reactivity at 473 K compared to 273 K is believed to lie in the increased rate of diffusion of adsorbed oxygen to subsurface sites on both the (0001) and (1010) surfaces [3], before passivation. Fig. 4 shows the variation
of the work function, $\Delta \phi$, as a function of oxygen exposure at 90, 293, and 473 K. The interpretation of these data is not straightforward, but the smaller decrease in $\Delta \phi$ at low exposures and the larger increase at high exposures, at 90 K, both indicate less adsorption into subsurface sites [3]. By contrast the larger negative values of $\Delta \phi$ at 473 K indicate more extensive subsurface absorption, leaving a Zr surface that can adsorb oxygen [3]. More problematical, is the microscopic origin of the very high reactivity at 90 K. The oxygen uptake rate at 90 K remains high and almost constant until the surface has been completely covered by about 10 Å of oxide at $\sim 4$ L exposure (Fig. 3). This probably relates to the longer residence time of oxygen at this temperature, permitting diffusion in a molecularly bonded layer to reactive sites, but it is also necessary to postulate a disordered surface to permit the growth of oxide films of the observed thickness. The uptake rate then decreases very quickly and reaches zero at an oxide thickness of about 12 Å. It seems that when the oxide is less than 10 Å thick it permits rapid passage of atoms to/from the Zr substrate beneath the oxide resulting in the formation of “new” oxide. In other words, a critical thickness of oxide, $\sim 12$ Å at 90 K, is necessary to prevent further oxidation. Below this critical thickness the oxide affords almost no protection.

The coverage of oxygen (strictly speaking, the areal density) shown on the left Y-axis in Fig. 3 was measured by the $^{16}$O(p, a)$^{13}$N nuclear reaction. The thickness of oxide shown on the right Y-axis is only for oxidation at 90 K and is computed from the NRA coverage data based upon assumptions listed below.

The Auger data in Fig. 5 show the Auger peak-to-peak intensities of O(KLL), Zr(MNN), Zr(MNV)$_m$ and Zr(MNV)$_s$, corresponding, respectively, to oxygen, Zr in metal (MNN) and (MNV)$_m$ Auger transition) and Zr in oxide during the initial oxidation at 90 K ($<30$ L). We use the method proposed in our previous paper [3], utilizing Eq. (1) to analyze the intensities as a function of coverage:

$$d = -\lambda \cos \theta \times \ln [I/[Zr(MNV)_m]/I/[Zr(MNV)_s]^0].$$

Fig. 5. Intensities of the indicated Auger transitions as a function of oxygen exposure at 90 K. Three stages are: (1) adsorption, (2) surface migration and growth of oxide, (3) saturation.

where $d$ is the thickness of oxide; $I/[Zr(MNV)_m]$ and $I/[Zr(MNV)_s]^0$ are the Auger electron intensities of Zr(MNV)$_m$ from the oxide-covered sample and the sample with no oxide at about 1 L oxygen exposure (Fig. 5), respectively; $\lambda$ and $\theta$ are the escape depth of Zr(MNV)$_m$ Auger electrons and the escape angle, which are 5.3 Å and 42$^\circ$, respectively. At 90 K the oxide growth appears to occur layer-by-layer: based on this, the thickness of oxide calculated from the Auger data through Eq. (1), is in good agreement with that obtained from the absolute coverage results if we make the following approximations: all the incoming oxygen atoms react with Zr atoms and are dissolved in/on the Zr metal at exposures below 1 L, producing ZrO$_2$ at exposures above 1 L; the thickness of oxide was calculated from the absolute oxygen coverage less the coverage at 1 L, then divided by the density of ZrO$_2$. We found no evidence in our data for the presence of substoichiometric Zr-oxides, although Jungblut et al. reported [23] that a small amount of substoichiometric Zr-oxide, ZrO$_x$ ($x > 1$), is probably present in the interface between ZrO$_2$ and Zr. The presence of up to $\sim 10\%$ would not affect the major conclusions. The Zr Auger spectra can be readily interpreted in terms of only ZrO$_2$ in the region in which oxide is formed [3].
Three stages of interaction can be seen from the results at 90 K illustrated in Fig. 5; the demarcations shown are intended as general guides to the eye. The first region, chemisorption (1), is clearly delineated by the absence of an Auger transition from oxidized Zr. The second, nucleation and growth of oxide (2), and the third, saturation (3), are not so readily distinguished, but effective saturation is achieved at 90 K by \( \geq 10 \) L. Saturation was not achieved at 293 or 473 K even up to 100 L exposure (AES results are not shown in this paper). Less oxide is formed at the two higher temperatures than at 90 K for equal exposures, which may be related to the faster diffusion of oxygen into the bulk. These results are very similar to the results previously obtained on the Zr(0001) surface in this laboratory [3].

It was found that a \((2 \times 4)\) superstructure was produced by chemisorption of oxygen before the formation of oxide. An oxygen exposure of 0.2 L to the Zr(1010)-(1 \times 4) surface at 90 K resulted in an increase in the intensity of background of the LEED pattern. Upon heating this surface to 473 K, followed by cooling to 90 K, the additional diffuse fractional order spots appeared. No change of O(4KL) Auger signal was detected with heating to 473 K, indicating that the oxygen atoms could only be moving in the surface region to find more stable locations, resulting in the observed superstructure. With increasing exposure, the additional spots became sharper and brighter, reaching their maximum intensity at an exposure of about 0.6 L. These additional spots, together with the \((1 \times 4)\) LEED pattern on the clean surface, formed a \((2 \times 4)\) pattern (Fig. 6), which indicated the new superstructure had double periodicity in \((1210)\) direction compared to the clean surface, but did not change periodicity in \((0001)\) direction. The additional spots then became diffuse at exposures over 0.6 L and completely disappeared at an exposure of 1 L. Since no Zr(MNV), peak was detected we believe that the \((2 \times 4)\) phase is a chemisorption structure. The coverage of oxygen at 0.6 L exposure was about \(8 \times 10^{14}\) atoms/cm\(^2\) (Fig. 2). If a unit cell of \((2 \times 4)\) only contains one oxygen atom, the oxygen coverage at 0.6 L of \(8 \times 10^{14}\) atoms/cm\(^2\) may correspond closely to an O-to-Zr surface atom ratio of 0.5 for the Zr(1010)-(1 \times 4) clean surface. The sign of the work function change in the initial reaction stage when the \((2 \times 4)-O\) superstructure was formed was negative (Fig. 4), which is consistent with a subsurface location for the oxygen atoms, similar to the conclusions on the Zr(0001) surface. The location of oxygen atoms in the subsurface region will also be invest-

---

**Fig. 6**: \((2 \times 4)\) LEED pattern from the Zr prism plane exposed to oxygen for 0.6 L at 90 K and then annealed at 473 K. Picture was taken at \(E_p = 45\) V.
tigated by NRA under channeling conditions and by angle-resolved Auger spectroscopy.

The \( (1 \times 4) \) superstructure was still visible even when the additional spots had completely disappeared after exposure over 1 L. For exposures of 5 L (when the thickness of oxide has reached 10 Å), a faint and diffuse \( (1 \times 4) \) pattern could still be recognized. It seems that either the oxide retains the \( (1 \times 4) \) superstructure; or patches of bare Zr surface remain. At saturation, the fractional order beams were not detectable above background.

3.3. The dissolution of oxide

It is known that oxide dissolves into bulk Zr when the sample is heated to high temperature.

![Graph showing diffusion coefficients](image)

**Fig. 8. Comparison of the diffusion coefficients of oxygen in Zr single-crystal along the (1,1/2,-1/2,1,0) direction \( D_1 \) [37] and \( D_2 \) [26] and the diffusion coefficients \( \Theta \) from the isothermal experiments in this work.**
In order to examine the major factor controlling oxide dissolution (oxide dissociation or oxygen diffusion into the bulk), an isothermal heating experiment was performed. The experiment involves monitoring the AES signals from an oxide layer as the sample was heated to and held at a variety of temperatures. Each data set gives a value of the diffusion coefficient at the particular temperature. The bulk O diffusion coefficients obtained from previous work [26,27] by methods such as internal friction were compared with the apparent "diffusion coefficient" calculated from the results of isothermal heating experiments by using a formula deduced from a model as described below.

Fig. 7 shows schematically the oxide dissolution process on Zr. If the dissolution of oxide is controlled by diffusion of oxygen in the bulk, from Fick's law, the distribution of oxygen in the bulk will be

$$C(x, t) = C_i \left[ 1 - \text{erf} \left( \frac{x}{2(Dt)^{0.5}} \right) \right].$$  \hspace{1cm} (2)

where $C_i$ is the oxygen concentration at the metal-oxide interface (which is 29% (a/a) from the phase diagram [28]). $D$ is the diffusion coefficient of oxygen along the direction perpendicular to the surface, assuming $D$ is constant with respect to the concentration, $t$ is the experimental time and the origin of $x$ is always taken at the interface. The flux of oxygen atoms can then be expressed by

$$J(x, t) = C_i \left( \frac{D}{\pi t} \right)^{0.5} \exp \left( -\frac{x^2}{4Dt} \right).$$  \hspace{1cm} (3)

The oxygen atoms dissolved from the oxide into the bulk is given by

$$M(t) = 2C_i \left( \frac{Dt}{\pi} \right)^{0.5}.$$  \hspace{1cm} (4)

The diffusion coefficient can be obtained from the plot of $M(t)$ versus $t^{0.5}$. If the rate-controlling factor is the diffusion of oxygen in Zr, the diffusion coefficient should be consistent with the published results.

The isothermal dissolution of oxide experiment was performed in the following manner. First, the Zr sample was exposed to oxygen at 90 K for 20 L. An oxide film of thickness 12.4 Å has been well established from the NRA and AES results (Figs. 3 and 4). The sample was then rapidly heated, at a rate of 100 K/s, to the chosen temperature and then held at that temperature. The Auger signals of zirconium and oxygen were recorded during the entire experiment. The thickness of oxide could be obtained from the Auger signal through Eq. (1).

Six temperatures, 573, 623, 648, 673, 698 and 723 K, were chosen for the isothermal oxide dissolution experiments. Fig. 8 illustrates $M(t)$, the quantity of oxygen dissolved into the bulk versus annealing time. The oxygen diffusion coefficients calculated at these six temperatures, using Eq. (4), are listed in Table 1. They are compared with the diffusion results taken from previous work in Fig. 9. The $D_o$ are 0.0661, 0.0442 and 0.0307 cm$^2$/s and the $E$ are 44000, 42387 and 43807 cal/mol for the results of Ritchie and Atkins [27], and Li et al. [26] for the (1010) surface, and for the (1010) surface in this work, respectively. The reasonable agreement in absolute magnitude of $D_o$ and activation energy indicates that the diffusion of oxygen into the bulk is the major rate-controlling factor for the dissolution of oxide.

4. Summary

It was found that the clean Zr(10\overline{1}0)-(1 x 1) surface produced by Ar-ion sputtering at 90 K and annealing to $T \leq 773$ K is metastable. At temperatures above 773 K, a reconstructed Zr(10\overline{1}0)-(1 x 4) surface is produced which is then stable at all temperatures 90 < $T$ < 1100 K. Exposure of the reconstructed surface to oxygen first produced a chemisorbed layer (which exhibited a (2 x 4) superlattice at room temperature or above), followed by oxide growth. At 90 K on the reconstructed (1 x 4) surface, the sticking coefficient remains high to coverages of several monolayers, the film becoming passive at a thickness of 12.4 Å. Passivation is not observed for exposures < 100 L at 293 and 473 K, probably because of the enhanced O diffusion in the surface region. Isothermal experiments indicated that the dissolution rate of oxide on the Zr surface was con-
trolled by oxygen diffusion into the bulk Zr and not by oxide dissociation.

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References

Adsorption kinetics accompanied by adsorbate diffusion into the solid

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Abstract

General equations are derived for describing the kinetics of adsorption accompanied by adsorbate diffusion into the solid. The main attention is focused on the case when the potential wells corresponding to the adsorbed overlayer are much deeper compared to those for the bulk. As an example, the kinetics of the deuterium uptake by Zr(0001) is analyzed in detail.

Keywords Adsorption kinetics, Diffusion and migration. Hydrogen; Low index single crystal surfaces. Models of surface kinetics; Zirconium

1. Introduction

Adsorption kinetics are governed first of all by the coverage dependence of the sticking coefficient, which is connected with details of the distribution of adparticles on the surface and may be affected by precursor states and promoters [1–3]. At finite coverages, adsorption kinetics depend also on other rate processes possible in the adsorbed overlayer. In the present paper, we will consider the effect of adsorbate diffusion into the solid on the kinetics of adsorption.

2. General kinetic equations

The problem we will solve is formulated as follows. First, the substrate is free of any species both on the surface and in the bulk (i.e., we do not analyze segregation). Adsorption starts at t = 0. No desorption occurs at t > 0. Adsorbed particles are able to migrate from the surface into the bulk and back. The gas-phase pressure and temperature are assumed to be constant at t > 0. Our goal is to calculate the time dependencies of the surface coverage and the amount of particles trapped into the solid.

If diffusion from the surface into the bulk is not accompanied by formation of close-packed compounds (islands or grains) in the adsorbed overlayer or in the subsurface region, the jumps of particles between layers can be described by the following equations

\[ \frac{d\theta_i}{dt} = k_{P} - k_{01}\theta_i - k_{10}\theta_i, \quad (1) \]

and

\[ \frac{d\theta_i}{dt} = k_{i-1,1}\theta_{i-1} - (k_{i-1} + k_{i+1})\theta_i + k_{i+1,1}\theta_{i+1}, \quad (2) \]

with the initial conditions \( \theta_i(0) = 0 \) and \( \theta_i(0) = 0 \), where \( \theta_i(t) \) is the surface coverage, \( \theta_i(t) \) (i ≥ 1) the coverages of the bulk layers, \( P \) the gas-phase pressure, \( k_s \) the adsorption rate constant dependent on \( \theta_i \), and \( k_{P} \),

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the rate constants for the transitions from layer \( j \) to layer \( i \), dependent in general on coverages \( \Theta_i \) and \( \Theta_j \) due to lateral interactions and saturation (such a dependence occurs at least for the surface layer, i.e., for \( k_{in} \) and \( k_{jn} \), if \( \Theta_j \) is not low, and may in principle occur for one or several subsurface layers as well). The type of approximations which can be used for solving Eqs. (1) and (2) depends on the behaviour of the potential energy for diffusion. If diffusion into the bulk is energetically favourable, the transitions from the surface into the bulk are in fact irreversible (because \( k_{0i} > k_{ij} \)) and the surface coverage satisfies the following equation

\[
\frac{d\Theta_i}{dt} = k_{1i} - k_{0i}\Theta_i. \tag{3}
\]

This equation can be easily integrated.

If the potential wells corresponding to the adsorbed layer are the same (or almost the same) as in the bulk, Eqs. (1) and (2) cannot be simplified and as a rule should be solved numerically. We will not analyze this case in detail because usually the potential wells on the surface are quite different compared to those in the bulk.

Our attention will mainly be focused on the situation when the surface potential wells are much deeper than the potential wells in the bulk. This case is of particular interest because it corresponds to many real systems (e.g., to hydrogen adsorption on different metals [4]).

If the potential wells on the surface are deep, the particles which were able to escape from the surface potential wells may easily be trapped again into these wells. Thus, it is clear that the surface layer and several adjacent layers should be in quasi-equilibrium already at the early stages of the adsorption kinetics (see Eq. (6) below). Moreover, the coverages corresponding to the subsurface and bulk layers will always be low compared to the surface coverage. In addition, the particles which have escaped from the surface will be distributed in many bulk layers. Taking into account all these facts, we can simplify considerably the analysis of Eqs. (1) and (2) (by analogy with the theory of surface segregation [5]). In particular, the rate equations for the bulk layers can be replaced by the diffusion equation

\[
\frac{\partial \Theta_i(x,t)}{\partial t} = D \frac{\partial^2 \Theta_i(x,t)}{\partial x^2}. \tag{4}
\]

with the following initial and boundary conditions

\[
\Theta_i(x,0) = 0, \tag{5}
\]

\[
\alpha_i(\Theta_i) \frac{\partial \Theta_i(x,t)}{\partial x} = \Theta_i, \tag{6}
\]

\[
-\frac{D}{a} \frac{\partial \Theta_i(x,t)}{\partial x} \bigg|_{x=0} = J, \tag{7}
\]

where \( D = a^2 k \) is the coefficient of diffusion in the bulk, \( a \) the lattice spacing, \( k \) the jump rate for the bulk layers (i.e., \( k = k_{0i}, \) for \( i \gg 1 \)), \( \alpha_i(\Theta_i) \) the equilibrium constant corresponding to a given value of \( \Theta_i \), and \( J \) the diffusion flux (per site) near the surface (at \( x = 0 \)).

Both the boundary conditions above describe quasi-equilibrium between the surface and several adjacent layers. In particular, condition (6) yields the ratio between the surface coverage and coverages of the neighbour bulk layers at quasi-equilibrium Condition (7), indicating that the number of particles escaping from the surface per unit time is just equal to the diffusion flux near the surface, reflects a kinetic aspect of quasi-equilibrium.

Formally, the necessary condition for applicability of the quasi-equilibrium approximation involves the relative time scales of adsorption and diffusion. In particular, the time scale for adsorption should be larger than that for jumps from the bulk to the surface. Really, however, this condition is not important because it is not fulfilled the bulk uptake is low (in the latter case, it does not matter if we assume or not quasi-equilibrium between the surface and subsurface layers, because anyway the bulk uptake calculated is negligible). A deeper analysis indicates that the quasi-equilibrium approximation described above is correct if the potential barrier between the surface and the first bulk layer is not too large, and diffusion from the bulk to the surface is not limited by this barrier (see the discussion in Ref. [6]). If the potential barrier is high and the jumps between the adsorbed and first bulk layers are suppressed, one may employ the opposite approximation assuming that all the bulk layers are in equilibrium and that there is no equilibrium between the surface and subsurface layers. In the latter case, the kinetics of adsorption accompanied by diffusion into the bulk will be described by one or two ordinary differential equations [7], e.g., by Eq (3) (provided that the bulk concentration is low, and the jumps from the first bulk layer to the surface are negligible)
Applying conditions (6) and (7), one should also bear in mind that the properties of a few subsurface layers (e.g., the rate constants \( k_s \)) may be different compared to those of the deep bulk layers. If however the population of the subsurface region is low and they are in quasi-equilibrium with the adsorbed overlayer (as discussed above), a few layers adjacent to the surface is in fact not significant for describing the time dependence of the surface coverage. This is a reason why we employ the bulk equilibrium constant in Eq. (6) and the bulk diffusion coefficient in Eq. (7). Accordingly, the coordinate \( x = 0 \) corresponds to the subsurface layers which are close to the surface but already have the properties of the bulk layers (\( x = 0 \) is attributed to the first bulk layer only provided that all the bulk layers are equivalent).

The diffusion flux \( J \) in Eq. (7) should be calculated self-consistently with Eq. (1). In particular, \( J \) should be equal to the net flux of particles from the surface into the bulk. Accordingly, we can rewrite Eq. (1) as

\[
\frac{d\theta_s}{dt} = k_s(\theta_s) P - J \tag{8}
\]

A formal solution to Eq. (4) with conditions (5) and (7) is known to be

\[
\theta(x,t) = 2a \int_0^t g(x,t-t') J(x,t') \, dt'. \tag{9}
\]

where \( g(x,t) = \exp(-x^2/4Dt)/(4\pi Dt)^{1/2} \); is the Green function. Substituting the latter expression into Eq. (9), setting \( x = 0 \), and employing condition (7), we have

\[
\theta_s(\theta_c) = \int_0^t \frac{a}{\pi D(t-t')}^1 J(x,t') \, dt'. \tag{10}
\]

Integrodifferential equations (8) and (10) derived above make it possible to calculate the time dependence of the surface coverage and the diffusion flux from the surface into the solid. Integration of these equations is however rather difficult (see the discussion of a similar problem in Ref. [6]). To avoid cumbersome numerical calculations, we can employ the steady-state approximation in order to evaluate the diffusion flux \( J(t) \); (this approximation is reasonable because the kinetics of diffusion is rather slow). In particular, taking into account that the typical diffusion length is given by

\[
L(t) = (Dt)^{1/2}, \tag{11}
\]

we can neglect diffusion into the region \( x > 2L(t) \), i.e. we can consider that \( \theta(x,t) = 0 \) at \( x \geq 2L(t) \). For \( 0 \leq x \leq 2L(t) \), the steady-state solution to Eq. (4) with the boundary condition (6) is

\[
\theta(x,t) = [1 - x/2L(t)] \theta_s/\alpha(\theta_c). \tag{12}
\]

Substituting this expression into Eq. (7), we have

\[
J = D\theta_s/[2a \pi L(t) \alpha(\theta_c)]. \tag{13}
\]

Then, Eq. (8) can be rewritten as

\[
\frac{d\theta_s}{dt} = k_s(\theta_s) P - D\theta_s/[2a \pi L(t) \alpha(\theta_c)]. \tag{14}
\]

or, employing expression (11) for \( L(t) \),

\[
\frac{d\theta_s}{dt} = k_s(\theta_s) P - (D/t)^{1/2} \theta_s/[2a \pi \alpha(\theta_c)]. \tag{15}
\]

This equation can be easily integrated.

Another approximation for \( \theta(x,t) \) can be constructed by employing the time-dependent solution of Eq. (4) corresponding to a given current coverage in the subsurface region (see, e.g., Section 7.1 in Ref. [2])

\[
\theta(x,t) = \theta_s/\alpha(\theta_c) \text{ erfc} \left( x/2L(t) \right). \tag{16}
\]

According to this equation, the diffusion flux near the surface is given by

\[
J = D\theta_s/[\sqrt{\pi} a L(t) \alpha(\theta_c)]. \tag{17}
\]

The latter expression differs from Eq. (13) by the factor \( 2/\sqrt{\pi} \). This factor characterizes in fact the accuracy of the approximations outlined above for calculating the absolute value of the bulk coverage. The accuracy of the time dependence of the flux \( J \) and of the absolute value of the surface coverage is of course much better.

The total uptake is by definition a sum of the surface and bulk uptakes,

\[
U_t = U_s + U_b. \tag{18}
\]

If the uptake is calculated per site, we have

\[
U_s = \theta_s \tag{19}
\]

and (from Eq. (12))

\[
U_s = [L(t)/a] \theta_s/\alpha(\theta_c). \tag{20}
\]

Substituting the latter two expression into Eq. (16) yields

\[
U_t = (1 + L(t)/\alpha(\theta_c)) \theta_s. \tag{21}
\]
To apply Eqs. (15) and (18), we need explicit expressions for the adsorption rate constant \( k_0(\theta_0) \) and the equilibrium constant \( \alpha(\theta) \). The simplest power-law and mean-field expressions for these constants are

\[
k_0(\theta_0) = k_0^0(1 - \theta_0)^n,
\]

and

\[
\alpha(\theta) = \exp\left[ (\Delta E - A\theta_0)/T \right] (1 - \theta),
\]

where \( \Delta E - A\theta_0 \) is the heat of segregation \( A\theta_0 \) is the contribution of the adsorbate–adsorbate interactions. The Boltzmann constant in Eq. (20) and below is omitted, i.e., \( k_B = 1 \).

Using Eqs. (15), (19) and (20), it is possible to obtain an asymptotic expression for the total uptake at \( t \to \infty \). With increasing time, if the temperature is not too low, the adsorption rate in Eq. (15) rapidly becomes almost equal to the diffusion flux (i.e., the diffusion into the bulk yields the main contribution to the uptake rate). In this case, one can employ the steady-state approximation for Eq. (15). With expressions (19) and (20), Eq. (15) yields

\[
(1 - \theta) \approx r^{-1/2(n-1)},
\]

and accordingly (see Eq. (20))

\[
\alpha(\theta) \approx r^{-1/2(n-1)}.
\]

Substituting the latter relationship into Eq. (17), we get

\[
U_0 = L(1)/\alpha(\theta) \approx r^{(n-2)/(2n-1)}.
\]

For \( n = 1, 2 \) and 3, the exponent in this expression is equal to 3/4, 2/3 and 5/8, respectively.

3. Application

As an example of the application of the equations derived above, we consider the kinetics of deuterium adsorption on a Zr(0001) surface. This process has been recently studied by employing nuclear reaction analysis (NRA), dynamic and static secondary ion mass spectroscopy (SIMS), and Auger electron spectroscopy [8]. The absolute deuterium uptake was determined by NRA which is able to measure the total amount of deuterium from the surface up to a depth of \(~0.25\) nm. The time dependence of the surface coverage was monitored by static SIMS calibrated against NRA. The key observations obtained at room temperature are as follows. The initial sticking coefficient is high, \( S_0 = 0.38 \pm 0.16 \). During adsorption, the surface coverage rapidly reaches \(~0.75\) ML (here 1 ML = Zr monolayer = \(1.11 \times 10^{15}\) atoms per \(\text{cm}^2\)) and then is almost constant at exposures above \(~5\) L (1 L = \(10^{-6}\) Torr·s). The uptake rate, decreasing with increasing exposure, does not expire at \(~5\) L, i.e., the uptake does not saturate in this case but instead it slowly increases (up to \(~1.3\) ML at \(~40\) L). With increasing temperature, deuterium diffuses from the surface into the solid (no D₂ desorption was detected).

The scheme proposed [8] to interpret the results observed includes (i) dissociative adsorption of D₂ on empty sites and (ii) direct trapping of deuterium into the solid during collisions of D₂ molecules with the surface regions covered by deuterium. The second step, introduced in order to describe the increase in the uptake at exposures above \(~5\) L, makes it possible to fit the measured kinetics. Physically, however, this step is not quite realistic. Our goal is to reinterpret the former room-temperature results [8] and also to discuss the new experimental data, obtained at 200 and 350 K (see Figs. 3 and 5), by employing a more common mechanism of the uptake, including dissociative adsorption and adsorbate diffusion from the surface into the bulk.

An analysis of the kinetic data for the D/Zr(0001) system is complicated by two factors. The first one is connected with the background hydrogen (or deuterium) which is always present in Zr. Our studies however showed that, if we prepare a clean surface and then measure the hydrogen or deuterium segregation (without adsorption) at 200–350 K, the amount of H or D segregated on the surface during the time typical for the adsorption kinetics is negligible. For this reason, in the following we do not take into account the background hydrogen or deuterium in our calculations.

The second factor complicating interpretation of the deuterium adsorption kinetics on Zr is connected with the possibility of hydride formation on the surface or in the bulk (employing the term “hydride”, we bear in mind both H–Zr and D–Zr compounds). The terminal hydrogen solubility in Zr is given by

\[
C_0(\text{ppm}) = C_0 \exp(-\Delta H/T),
\]

where \( C_0 = 1.6 \times 10^5 \), and \( \Delta H = 9.0 \) kcal/mol is the apparent difference between the partial molar heat of solution of hydrogen in Zr and the hydride phase [9]. At 200–350 K, the total hydrogen and deuterium concentration in the crystal (i.e., the ratio of the total amount of H and D loaded into the sample to its volume) is much higher than \( C_0 \), and accordingly the
hydride formation is thermodynamically favourable.

Discussing the hydride formation on the surface, one needs to distinguish between "chemisorbed hydrogen or deuterium" and "surface hydride". By analogy with the bulk, formation of the surface hydride is expected to be accompanied by the change of type of the metal lattice near the surface (in the bulk, the hcp lattice of α-Zr is replaced by the fcc lattice of δ-hydride [9]). Also by analogy with the bulk, the hydride formation on the surface seems to be described in terms of the theory of first-order phase transitions. On the other hand, for chemisorbed hydrogen or deuterium, the arrangement of metal atoms near the surface is expected to be qualitatively the same as in the case of a clean surface.

At present, it is not quite clear if the surface hydride is formed on the (0001) face of Zr during hydrogen or deuterium adsorption at relatively low temperatures. There are at least two factors against this route on the (0001) face. (i) The hydride formation is known to occur preferably on more open faces [9]. (ii) This process, if it occurs, should manifest itself in the adsorption kinetics. Taking into account that the local hydrogen or deuterium coverage in hydride islands is high, one might expect that the kinetics of adsorption accompanied by formation of the surface hydride is described by Eq. (19) with $n = 1$ (this exponent holds if (i) adsorbed hydrogen or deuterium is primarily in the hydride phase, and (ii) adsorption occurs mainly on the sites that are free of hydride). The measurements indicate however that $n = 3$ (see below). The latter exponent does not correspond to island formation.

Considering the comments above, we neglect the hydride formation and use the formalism presented in Section 2 in order to describe the time dependence of the surface coverage and evaluate the uptake by deep bulk layers. The equations employed are based on the assumptions that the subsurface region is in quasi-equilibrium with the adsorbed overlayer and the population of this region is low. These assumptions are reasonable for calculating the diffusion flux from the surface to the bulk even if the properties of a few subsurface layers are different compared to those in the bulk (see the discussion in Section 2). If however the latter really occurs (e.g., the potential well corresponding to a few subsurface layers are much deeper than in the bulk), the model may underestimate the uptake connected with the subsurface region. For this reason, we focus our attention on the time dependence of the surface coverage. Then, comparing the calculated and measured total uptakes, it is possible to make some conclusions about the role played by the subsurface layers in the observed kinetics.

To describe dissociative adsorption of deuterium, we use Eq. (19) with $n = 3$

$$k_d^n = S_0 (2 \pi m kT)^{-1/2} / N_f,$$

where $m$ is the D$_2$ mass, $S_0 = 0.38$ the measured sticking coefficient, $T = 300$ K the gas-phase temperature, and $N_f$ is the absolute deuterium coverage corresponding to saturation (i.e., to $\Theta = 1$).

Simulations with $n = 3$ fit the experiment a little better than with $n = 2$ (the latter value corresponds to the Langmuir model of dissociative adsorption with random distribution of particles in the adsorbed overlayer). The obtained rather strong dependence of the sticking coefficient on coverage ($n = 3$) may be connected with repulsive adsorbate-adsorbate interaction resulting with increasing coverage in a rapid decrease of the probability to find a pair of empty nearest-neighbour sites [2].

The measurements indicate that $N_f \geq 0.75$ ML (1 ML is defined above). Our preliminary calculations have shown that it is reasonable to employ $N = 0.9$–$1.1$ ML. The results presented below have been obtained with $N_f = 1$ ML.

For the deuterium diffusion coefficient, we employ the Arrhenius expression, $D = D_0 \exp(-E_d / T)$, with
Fig. 2. Kinetics of deuterium adsorption on Zr(0001) as a function of exposure calculated at $T = 300 \text{ K}$ and $P = 10^{-6} \text{ Torr}$. $U_\alpha$, $U_\beta$, $U_t$ and $U_b$ correspond to the surface, bulk, total and NRA uptakes, respectively.

the "normal" pre-exponential factor, $D_0 = 10^{-3} \text{ cm}^2/\text{s}$, and the measured activation energy, $E_a = 8.3 \text{ kcal/mol}$ [8] (in addition, we assume $D_0/\alpha^2 = 10^{13} \text{ s}^{-1}$).

The segregation heat for the Zr(0001) face measured at low coverages is $\Delta E = 9.5 \text{ kcal/mol}$ [10].

After the specification above, we have only one free parameter, $A$, describing the coverage dependence of the segregation heat (Eq. (20)). If the heat of segregation is independent of coverage ($A = 0$), the model predicts that at room temperature the deuterium uptake by deep bulk layers is in fact negligible. In this case, one can in principle attribute the peculiarities of the observed kinetics to diffusion into the subsurface layers. Such a possibility cannot be ruled out definitively. On the other hand, we can expect, as pointed out above, that the subsurface layers are in quasi-equilibrium with the adsorbed layer. In the latter case, it is not quite clear why the surface coverage is almost constant at exposures $> 5 \text{ L}$ and at the same time the uptake continues to increase.

If we take into account the coverage dependence of the segregation heat (Eq. (20) with $A 
eq 0$), the observed kinetics can be explained more naturally as a balance between adsorption and diffusion into the solid. By analogy with thermal desorption of chemisorbed particles [3], the value of $A$ in Eq. (20) is expected to be in the range from $-5$ to $10 \text{ kcal/mol}$ ($A > 0$ corresponds to repulsive adsorbate-adsorbate interaction).

With our set of the other parameters, the results of calculations are in reasonable agreement with the experiment if $A = 3.5 \text{ kcal/mol}$.

To compare the experimental data and simulations, we note that at 300 K the deuterium diffusion length, given by Eq. (11), is much larger than the NRA depth already at early stages of the adsorption kinetics. For this reason, the total uptake calculated by employing Eq. (18) cannot be directly compared with the NRA data. The uptake $U_m$ corresponding to NRA measurements has been calculated as a sum of the surface coverage and the bulk coverage (Eq. (12)) integrated from $x = 0$ up to 0.5 $\mu\text{m}$ (two NRA depths).

Fig. 3 shows the measured and calculated deuterium uptake at 300 K and exposures up to 8 L. The model predicts that diffusion into the solid is almost negligible at exposures $\leq 4 \text{ L}$. In this region, the measured and calculated NRA uptakes are in good agreement. At exposures $> 5 \text{ L}$, the rates of adsorption and diffusion into the solid are close, and the calculated surface coverage is almost constant ($0.63 \leq U_t \leq 0.69 \text{ ML}$ at exposures of 8–50 L, as shown in Fig. 2). This result is in agreement with the SSIMS data. The total uptake predicted is rather large (about 3 ML at 50 L). For the NRA uptake, the model however yields $U_m = U_t = 0.75 \text{ ML}$ at exposures of 30–50 L. The latter disagreement with the NRA measurements ($U_m = 1.3 \text{ ML}$ at 40 L) can be connected with the extra deuterium uptake in the subsurface region as we have discussed in the beginning of this section.

Fig. 3. Deuterium uptake on the Zr(0001) surface calculated at $T = 200 \text{ K}$ and $P = 10^{-6} \text{ Torr}$ (diffusion into the solid in this case is negligible, $U_t < 0.01 \text{ ML}$). Circles show the measured NRA uptake. In the experiment, pressure was $10^{-6} \text{ Torr}$ at exposures of 1–3 L. At lower and higher exposures, pressure was a little lower and higher, respectively. The latter is however not important for comparing the calculated and measured results.
The results shown in Figs. 1 and 2 have been obtained at 300 K. It is instructive to calculate the adsorption kinetics also at lower and higher temperatures. With decreasing temperature, the rate of diffusion decreases and accordingly the deuterium uptake by bulk layers decreases as well. In particular, the model predicts that the bulk uptake is almost completely negligible at 200 K (Fig. 3), i.e. \( U_m \approx U_m \approx U_m \approx U_m \). The calculated uptake is in a good agreement with the measured NRA uptake at exposures lower than 20 L. With further increase in exposure, the model yields a lower uptake compared to NRA.

With increasing temperature above 300 K, the bulk makes a dominant contribution to the deuterium uptake. In this case, the surface coverage rapidly reaches apparent saturation with increasing exposure due to balance between adsorption and diffusion into the solid (as it has been discussed above for 300 K). The apparent saturation coverage at higher temperatures may however be much lower than at 300 K. For example, at exposures \( \leq 50 \) L, the surface coverage saturates at \( \approx 0.52 \) and \( 0.36 \) ML as shown in Fig. 4 for 350 and 400 K, respectively.

The deuterium NRA uptake measured at 350 K is presented in Fig. 5 together with the NRA data obtained after deuterium adsorption followed by the surface sputtering (about 100 Å). The latter data correspond to the deuterium uptake by deep bulk layers (from the subsurface region up to 0.5 μm). The difference between the signals is attributed to the uptake by the surface and a few subsurface layers. From Fig. 5, one can conclude that at 350 K the uptake by deep bulk layers (up to 0.5 mm) is considerable, about 0.2 ML at 30 L. According to the model, this uptake, given by the difference between \( U_m \) and \( U_m \) is also about 0.2 ML at exposures of 20–50 L (Fig. 4a). On the other hand, the NRA uptake measured for the surface and a few subsurface layers, \( \sim 0.8 \) ML at 10–30 L, is larger than the calculated surface uptake, \( \sim 0.5 \) ML at 10–50 L. The latter seems to be connected with the extra deuterium uptake in the subsurface region.

Above, we have considered the hydrogen behaviour on the Zr(0001) surface. For comparison, it is worthwhile to mention that the kinetics of hydrogen adsorp-
tion on the polycrystalline Zr surface have been explored in Ref. [11]. The kinetic scheme employed [11] to interpret the obtained experimental data is close to that used in our study. The energetic parameters are, however, different. In particular, the activation energy for hydrogen diffusion, segregation heat, and parameter \( A \) (Eq. (20)) are, respectively, as follows: 8.3 (11.0), 9.5 (1.3), and 3.5 (5.8) kcal/mol (the data from Ref. [11] are parenthetical).

4. Conclusion

Employing general equations derived for describing the kinetics of adsorption accompanied by adsorbate diffusion into the solid, we have considered two alternative scenarios of the deuterium uptake by Zr(0001).

(i) If the heat of deuterium segregation, 9.5 kcal/mol is independent of coverage \( (A = 0) \), the model predicts that at room temperature the deuterium uptake by deep bulk layers is in fact negligible. Thus, one can in principle attribute the special features of the observed kinetics only to diffusion into the subsurface layers. In this case, it is difficult however to understand why the measured surface coverage is almost constant at exposures \( > 5 \) L, and at the same time the uptake continues to increase.

(ii) If we take into account the coverage dependence of the segregation heat (Eq. (20) with \( A = 3.5 \) kcal/mol), the observed room-temperature kinetics can be naturally explained as a balance of adsorption and diffusion into the solid.

The latter scheme, however, underestimates the NRA uptake as it follows from comparing the results of measurements and calculations at 200–350 K. The disagreement may be connected with the extra uptake by a few subsurface layers. Thus, the potential wells for several subsurface layers seem to be considerably deeper than those on the bulk, and the total deuterium population of these layers may be comparable with that of the adsorbed overlayer.

In summary, our analysis indicates that deuterium diffusion both to the subsurface and deep bulk layers appears to play a role in the process under consideration.

Finally, it is reasonable to point out once more that the system under consideration is complex. In particular, we do not rule out that the observed kinetics of deuterium adsorption on Zr(0001) is affected by hydride formation.

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The study of hydrogen segregation on Zr(0001) and Zr(10\overline{1}0) surfaces by static secondary ion mass spectroscopy, work function, Auger electron spectroscopy and nuclear reaction analysis

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Abstract

The segregation of hydrogen on Zr(0001) and Zr(10\overline{1}0) surfaces was studied by static secondary ion mass spectroscopy (SSIMS), Auger electron spectroscopy (AES), work function measurement and nuclear reaction analysis (NRA). It was found that hydrogen has a strong tendency to segregate on these Zr surfaces. The heats of segregation, measured by SSIMS which was calibrated by NRA, are 10.1 kcal mol$^{-1}$ on Zr(0001) and 10.7 kcal mol$^{-1}$ on Zr(10\overline{1}0). The valence-band-related AES of Zr indicated that the modification of the Zr valence band by the segregation of hydrogen is similar to that resulting from the formation of surface hydride. This is connected with the strong tendency for hydrogen to segregate. The diffusion coefficients of hydrogen along (0001) and (10\overline{1}0) directions in a Zr single crystal were measured by the kinetics of surface segregation. It was found that the diffusion along (0001), $D = 0.034 \exp(-9565/RT)$ mm$^2$s$^{-1}$, is slower than that along (10\overline{1}0), $D = 0.173 \exp(-8887/RT)$ mm$^2$s$^{-1}$, where $R$ is the gas constant. This may be explained by the difference in the atomic density on (0001) and (10\overline{1}0) faces and the partition functions of the activated states in these two diffusion paths. It was found that dissolved oxygen enhances the diffusion of hydrogen.

Keywords: Hydrogen segregation, Nuclear reaction analysis, Static secondary ion spectroscopy; Hydrogen diffusion, Zirconium

1. Introduction

Surface or interface (grain boundary) segregation, the preferential enrichment of some components of a multicomponent system at a surface or interface (grain boundary), has attracted much attention [1]. This is an important phenomenon because of the significance of segregation in the determination of many material properties. The segregation of hydrogen at the zirconium surface is a typical example.

Due to the low nuclear absorption cross-section, high mechanical strength and excellent corrosion resistance at elevated temperatures, zirconium and its alloys play an important role in the nuclear industry [2]. It has been found that two types of major failure determine the lifetime of components containing Zr or its alloys: (1) delayed hydride cracking controlled by stress gradients around a flaw, and (2) a rapid cracking process through hydride "blisters" formed around a "cool" spot at the surface [3]. These failures are related to the formation of hydride, and therefore the bulk concentration of hydrogen in the as-received Zr-made components is kept well below the solubility limit of hydrogen in zirconium alloys. However, the concentration of hydrogen in Zr components can increase during operation through the ingress of hydrogen from the outside. Because of the large heat of segregation at the surface and interfaces of zirconium, and the high mobility in zirconium, hydrogen atoms often accumulate at the grain boundaries, surfaces of microcracks and cool spots on the surface. The formation of hydride is initiated at these locations because the concentration of hydrogen is much higher there than elsewhere. Cracking initiated at these locations can then occur under certain conditions. Hydrogen segregation is one of the most important stages leading to failure of Zr components.

Unfortunately, only a few reports have been published on this important problem [4-6]. This may be attributed to the difficulties in studying the segregation of hydrogen at zirconium surfaces. One difficulty involves the preparation of a clean Zr surface. Here, a "clean" surface means that the surface concentration of contaminants must be below 1%-2% of a mono-
layer during the entire experimental period. If this requirement cannot be fulfilled, the co-segregation of hydrogen with contaminants may change significantly the hydrogen segregation behaviour. The zirconium surface can be easily cleaned by Ar$^+$ ion sputtering, but maintaining a clean surface for longer times is relatively difficult. There are two types of contaminant which can be built up on the surface: (1) gases (mainly oxygen, carbon monoxide, water, etc.) adsorbed from the environment in the vacuum chamber; (2) segregants (mainly sulphur, phosphorus, iron, nickel, hydrogen, etc.) coming from the bulk. Zirconium and its alloys are very reactive materials with respect to these gases, and in order to keep the gas adsorption rate low enough, the base pressure in the vacuum chamber needs to be below $5 \times 10^{-11}$ Torr, which is readily attainable. It is more difficult to prevent segregation. Many segregates have very high heats of segregation, which lead to high surface concentrations, even though their bulk concentrations are as low as a few parts per million. In order to limit the segregation to a low level (for example, surface concentration below 1%–2% of a monolayer), a reduction of the concentration of the segregant in the bulk is necessary. An efficient method has been developed in our laboratory to achieve this (see Section 2).

Another difficulty is the quantitative measurement of surface hydrogen. Since it is impossible to detect surface hydrogen by most electron spectroscopy techniques, such as static secondary ion mass spectroscopy (SSIMS) and high-resolution electron energy loss spectroscopy (HREELS), are available for the measurement of surface hydrogen. Although SSIMS is a sensitive technique for the detection of hydrogen, quantitative results are not easily achieved. In our laboratory, an ultrahigh vacuum chamber equipped with conventional surface techniques, including SSIMS, is on-line to a Van de Graaff accelerator. The absolute surface concentration of hydrogen measured by nuclear reaction analysis (NRA) allows the yields of secondary hydrogen ions detected by SSIMS to be quantified.

In a previous study [4], we have noted the observation of the segregation of H on the Zr(0001) surface. Due to the poor signal to noise ($S/N$) ratio of SSIMS using an Ar$^+$ ion beam, we were not able to monitor the surface concentration of hydrogen simultaneously with the occurrence of surface segregation. Therefore kinetic parameters were not obtained. In the present work, a Ca$^+$ ion beam was employed, which produces a higher $S/N$ ratio for the hydrogen ion ($H^+$) yields than that obtained using the Ar$^+$ beam ($H^+$). In this paper, the change in surface concentration of hydrogen on Zr(0001) and Zr(1010) during segregation at various temperatures is reported. The heat of segregation and certain thermodynamic and kinetic parameters are then derived. The binding situation of segregated hydrogen atoms with surface zirconium atoms is also discussed. Hydrogen diffusion was measured along the directions perpendicular to the (0001) and (1010) surfaces. The influence of high concentrations of oxygen on the diffusion of hydrogen was investigated.

2. Experimental details

2.1. General information

The experiments were performed in a two-level ultrahigh vacuum chamber equipped with low energy electron diffraction (LEED), work function measurement ($\Delta\phi$) and secondary ion mass spectroscopy (SIMS) on the upper level and Auger electron spectroscopy (AES) and nuclear reaction analysis (NRA) on the lower level. SIMS can be operated in the dynamic mode (DSIMS) or static mode (SSSIMS). The general experimental arrangement has been described previously [7]. The chamber was pumped by a baffled diffusion and Ti sublimation pumps allowing base pressures of less than $3 \times 10^{-11}$ Torr to be achieved. The two samples (with surfaces of Zr(0001) and Zr(1010) orientation) were cut from a 99.99% pure single crystal rod and oriented and polished to within $\pm 0.5^\circ$ of the basal or prism planes.

The segregation experiments were performed with two types of temperature control mode: linear heating or holding at a constant temperature. In the “linear heating” mode, the sample was heated to 650°C and held there for a few minutes to dissolve all the surface contaminants; it was then rapidly cooled to room temperature (about 50–100°C s$^{-1}$). As soon as room temperature was reached, the sample was heated to over 500°C at low constant rate (1°C s$^{-1}$). In the “holding mode”, the sample was rapidly cooled to the assigned temperature and then held. The “linear heating” mode was used to measure the heat of segregation and the “holding” mode to measure the diffusion coefficient. The accuracy of temperature control was better than $\pm 0.5^\circ$.

During the segregation experiments, the surface was monitored by SSIMS or work function measurement. The parameters used in SSIMS are described in Section 2.4. Work function measurements were performed using a Kelvin probe, characterized by a root-mean-square noise level of 1 mV at a time constant of approximately 100 ms. AES was used to monitor the change in valence-band-related Auger transitions from Zr atoms when hydrogen segregation was occurring. The AES results were obtained using a Perkin-Elmer Physical Electronics single-pass cylindrical mirror analyser (CMA) Auger spectrometer. Typical parameters for AES were 3 keV and 0.5 mA for the primary electron beam and 1 V for the modulating voltage.
NRA was employed to calibrate the SSIMS signal. The absolute hydrogen (using the \( ^{1}H \) isotope) coverage was measured using the \( ^{1}H(He, p)^{4}He \) reaction employing a 630 keV \( ^{4}He \) beam. The number of protons emitted from the sample was referenced to the proton yield from a \( Ta_{2}O_{5} \) target of known oxygen coverage in the same geometry using the \( ^{16}O(d, p)^{17}O \) reaction and the ratio of the cross-sections of these two nuclear reactions \([8-10]\). The accuracy of this method is \( \pm 5\% \).

2.2. The surface cleaning procedure

As mentioned above, there are two types of contaminant occurring on the surface: adsorbates and segregants. To remove the adsorbates, the samples were sputtered by a 3 keV \( Ar^{+} \) beam for about 30 min which removed most of the surface contaminants, and then heated to 650°C and held for 2 min to remove residual adsorbates into the bulk. This sputtering-heating procedure has been employed successfully to reduce the concentration of contaminants to below 1\%–2\% of a monolayer on the surface \([7]\).

Although the initial bulk concentrations of segregants in the single crystal are very low (S and P: a few parts per million; Fe and Ni: below 50 ppm), their surface concentrations can sometimes reach tens of percent through surface segregation \([11]\). It has been observed that Fe, Ni, S and P appear on the surface with hydrogen during the segregation experiments when the cleaning process has not been carried out. In order to prevent the "co-segregation" which will change significantly the segregation behaviour of hydrogen, reduction of the bulk concentrations of these segregants is necessary. It was found that an efficient way to achieve this is to utilize their own strong segregation behaviour. Depending on their diffusion coefficients and heats of segregation, each segregant has its own temperature at which segregation is most efficient. By employing temperature-programmed AES or SSIMS measurement, these can be easily determined. For example, for S and P this occurs at 800°C and for Fe and Ni at 600°C. The segregants were then removed from the surface by \( Ar^{+} \) etching at these temperatures until the surface concentrations of the segregants were reduced to levels undetectable by AES. Depending on the type of segregant and the initial bulk concentration, the sputtering at elevated temperatures usually took 1 h to tens of hours.

2.3 The determination of the bulk concentration of hydrogen

In order to measure the diffusion coefficient of hydrogen, its bulk concentration must be known (see Section 3.2). To prevent the formation of bulk hydride, the bulk concentration of hydrogen should be below the terminal solid solubility (TSS) which is below 50 ppm at room temperature \([12]\). It is difficult to measure such a low bulk concentration of hydrogen with reasonable accuracy. We obtained the bulk concentration by loading a known amount of hydrogen into a hydrogen-free sample. The as-received sample usually contained more than several hundred parts per million of hydrogen. In order to deplete the sample of hydrogen, a sputtering-heating cycling procedure was employed. The sample was heated to 250°C for \( Zr(0001) \) or 200°C for \( Zr(1010) \) and held for several tens of minutes to let the hydrogen atoms in the bulk migrate and segregate at the surface. The sample was simultaneously etched by an \( Ar^{+} \) ion beam to remove the segregated hydrogen immediately. The sample was then heated to 650°C and held for a few minutes to distribute the hydrogen uniformly over the entire sample, as sputtering at 200 or 250°C only depleted the hydrogen in the near-surface region. After several cycles of sputtering at 200 or 250°C and then at 650°C, it was found that the concentration of segregated hydrogen was reduced. This sputtering-heating cycling process was repeated until hydrogen segregation could no longer be detected. Since segregation was detectable after 1 ppm of hydrogen was loaded in the sample, we believe that the bulk concentration had been reduced to below 1 ppm when segregation was not detected.

The uptake of deuterium at various temperatures has been investigated by NRA \([13,14]\). It was observed that saturation was reached at \( -183°C \) if the exposure of deuterium was over 1.1L (1L = \( 10^{-4} \) Torr s). The saturation coverage is \( 6.9 \times 10^{15} \) atoms cm\(^{-2}\) on \( Zr(0001) \) and \( 9.1 \times 10^{14} \) atoms cm\(^{-2}\) on \( Zr(1010) \). Since the saturation coverage is mainly determined by the chemical properties of deuterium, it is reasonable to assume that the saturation coverage will be the same for hydrogen. The deuterium or hydrogen adsorbed at \( -183°C \) diffused into the bulk, rather than desorbed out of the sample, when the sample was heated. Therefore the amount of hydrogen loaded into the bulk on heating was equal to the total coverage on the entire surface of the sample. By repeating this exposure at \( -183°C \) and then heating to 650°C, the bulk concentration of hydrogen was gradually built up to a known value.

2.4. A non-destructive and quantitative measurement by SSIMS

SSIMS was the major surface technique used to measure the surface concentration of hydrogen in this work. Since its discovery in the 1970s by Bennin-ghoven \([15]\), SSIMS has been used as a unique technique for studying surface hydrogen. A very low ion beam density must be employed to allow only a few per cent of the irradiated surface area to be
disturbed by the primary ions during the entire measuring time. In this work, a primary Ca$^+$ beam with a density of about 4 nA cm$^{-2}$ was used, which only allows $1.1 \times 10^{12}$ Ca$^+$ ions per square centimetre to hit the surface during a typical experiment (500 s). The atomic density of a Zr surface is about $1 \times 10^{15}$ atoms cm$^{-2}$. One primary ion collides with more than one substrate atom when travelling in the substrate. In order to confirm that these collisions do not alter the behaviour of hydrogen segregation, the SSIMS results of hydrogen segregation were compared with those using a “non-continuous” SSIMS measuring mode. In our SSIMS experiments, the primary beam continuously bombarded the sample during the entire segregation experiment. The “non-continuous” mode involved switching the primary beam onto the sample after the segregation experiment had been in progress for a period of time. In this case, the data taken in the first few seconds were from a segregated surface without irradiation by the primary beam. It was found that the hydrogen segregation measured by the “non-continuous” mode is consistent with that from the continuous experiments, regardless of the segregation time before switching on the primary beam. This confirms that, although the primary beam continuously bombards the sample during the entire experiment, it does not change the behaviour of hydrogen segregation.

The SSIMS signals were calibrated by NRA to provide quantitative surface hydrogen analysis. The calibration procedure was performed as follows. The uptake of $^2$H$_2$ on the Zr surface at room temperature was measured by NRA. The uptake was also measured by SSIMS under the same exposure conditions (temperature and pressure). Fig. 1 shows these two results for the Zr(0001) surface. It can be seen from Fig. 1 that the hydrogen secondary ion yield is proportional to the absolute coverage obtained by NRA when the coverage is below $7 \times 10^{14}$ atoms cm$^{-2}$. For exposures over 4L, the uptake of $^2$H$_2$ increases (see NRA results), but the hydrogen secondary ion yields become saturated. It is known experimentally and theoretically [13,14,16,17] that adsorbed hydrogen atoms prefer to stay at the surface when the coverage of hydrogen is low. Due to the increase in the interatomic interactions of hydrogen atoms at the surface, some of the adsorbed hydrogen atoms diffuse into the bulk, populating the layers near the surface, when the surface coverage is high. NRA can detect hydrogen atoms located in the surface region to a depth of 0.5 μm [8]. The NRA results shown in Fig. 1 do not represent only the hydrogen on the surface, but the secondary ions in the SSIMS experiments originate only from the surface [15]. This is why the two results are no longer proportional to each other when the coverage exceeds $7 \times 10^{14}$ atoms cm$^{-2}$. A conclusion can be obtained from the results in Fig. 1: the yield of hydrogen ions in our SSIMS experiments is proportional to the surface concentration of hydrogen. It is known that segregants usually populate only the surface [1]; therefore the hydrogen yields detected by SSIMS during the segregation experiments are proportional to the concentration of segregated hydrogen. The surface concentration of hydrogen can thus be obtained from the SSIMS results by using the proportionality factor between NRA and SSIMS. Similar NRA and SSIMS experiments were performed on the Zr(1010) surface. Proportional behaviour was also observed in the low coverage region, but the proportionality factor was different from that on Zr(0001).

3. Results and discussion

3.1. The heat of segregation ($\Delta E$)

The main driving force for the segregation is the decrease in energy attained on formation of bonds between the segregated atoms and the substrate atoms on the surface. This decrease in energy is defined as the heat of segregation or segregation energy ($\Delta E$).

3.1.1. A general equation

A general equation for describing the surface segregation during linear heating has been recently derived [17]. This equation is integrated by taking into account the rapid increase in the diffusion coefficient with increasing temperature. If the surface coverage is lower than equilibrium, it will increase with increasing temperature due to surface segregation, reach a maximum, and finally decrease. In the higher temperature region, where the coverage decreases, the surface segregation reaches equilibrium. In this case, the dissolved atoms are no longer transported to the
surface or interface and the surface concentration of the segregant is related to the heat of segregation, the interaction of segregant atoms on the surface, the bulk concentration and the surface concentration itself

\[
\ln(\theta_s) = \frac{\Delta E_s}{RT} + \ln(1 - \theta_s)
\]

\[
- \ln\left(\frac{[p_{AA} \exp(\varepsilon_{AA}/RT) + 0.5p_{AO}]}{[p_{AA} + 0.5p_{AO}]^{0.5}}\right) + \ln(\theta_s)
\]

(1)

where \(\theta_s\) and \(\theta_b\) are the surface and bulk concentrations of the segregant respectively, \(\varepsilon_{AA}\) is the interaction energy between segregated atoms on the surface, \(p_{AA}\) and \(p_{AO}\) are the quasichemical probabilities for neighbour A-A or A-O pairs respectively, \(z\) is the number of nearest-neighbour sites for the segregated atoms on the surface, \(R\) is the gas constant and \(T\) is the sample temperature in kelvin. The first, second, third and fourth terms on the right-hand side of this expression describe the contributions of the heat of segregation, the surface concentration of the segregant, the interaction between segregated atoms on the surface and the bulk concentration of the segregant giving rise to the segregation respectively.

If \(\theta_s\) is small enough, the second and third terms are negligible, and we have

\[
\ln(\theta_s) = \frac{\Delta E_s}{RT} + \ln(\theta_s)
\]

(2)

Since the hydrogen secondary yield \(Y_h\) is proportional to the surface concentration of hydrogen when the coverage is low, \(\theta_s\) can be substituted by \(Y_h\)

\[
\ln(Y_h) = \frac{\Delta E_s}{RT} + \ln(\theta_s) + \ln(F_p)
\]

(3)

where \(F_p\) is the proportionality factor between \(Y_h\) and \(\theta_s\) \((Y_h = F_p \theta_s)\). Therefore \(\Delta E_s\) can be derived from the slope of the curve of \(\ln(Y_h)\) vs. \(1/R\) in the case of equilibrium segregation when the surface segregation concentration is low.

### 3.1.2. The determination of the heat of segregation (\(\Delta E_s\))

The sample, after the cleaning procedure, was heated to 650°C to dissolve completely all the contaminants (mainly hydrogen) into the bulk. The sample was then cooled to room temperature at a rate of 50–100°C s\(^{-1}\). The rapid rate of cooling prevents hydrogen segregation. As soon as the temperature reached room temperature, the sample was heated at a linear rate. The surface concentration of hydrogen was measured simultaneously by SSIMS. The heating rate must not be too fast in order to achieve equilibrium segregation. It also must not be too slow, which would result in a long experimental time and too high an exposure to the primary beam. As a compromise between these two considerations, 1°C s\(^{-1}\) was chosen in our experiments. The total time for a typical segregation experiment at a heating rate of 1°C s\(^{-1}\) was about 300–500 s. As has been indicated above, the primary beam did not change the behaviour of hydrogen segregation during the SSIMS experiments.

Fig. 2 shows the experimental results of hydrogen segregation on Zr(0001) and Zr(1010) surfaces measured by SSIMS during linear heating. The segregation behaviour on these surfaces is similar and consistent with that predicted by Eq. (1), except for the fact that the temperature region where segregation occurs is higher on Zr(0001) than on Zr(1010) by about 50–70°C. Fig. 2 shows that segregated hydrogen can be detected at 80°C on Zr(1010) and at 150°C on Zr(0001). Since the rate of segregation in the lower temperature region is controlled by the diffusion rate of hydrogen in the bulk, the surface concentration exponentially increases with increasing temperature in the initial stage (Fig. 2). The fact that the temperature at which segregation starts is lower on Zr(1010) than on Zr(0001) can be understood from the fact that the diffusion rate along the (1010) direction is faster than that along the (0001) direction (see Section 3.2). With a further increase in temperature, the net segregation rate starts to decrease and a maximum in the surface concentration of hydrogen is observed. Above this temperature \(T_m\), the surface concentration of hydrogen decreases due to the dissolution of segregated hydrogen back into the bulk. No hydrogen desorption from either surface could be detected by thermal desorption spectroscopy during the entire segregation experiment.

Eq. (2) is only valid for equilibrium segregation, where the surface concentration of hydrogen no longer changes at constant temperature. In order to find the temperature region where equilibrium segregation is reached, a step heating experiment was performed. The sample was linearly heated to above \(T_m\) and then held for a certain time at various temperatures to examine whether the surface concentration of hydro-
The results for the Zr(10\overline{1}0) surface are shown in Fig. 3, in which the equilibrium segregation was found to occur at temperatures above 260°C. The corresponding temperature on Zr(0001) is above 300°C. It is clear that, at the higher temperature, the diffusion rate is sufficiently rapid to be no longer the controlling factor for segregation. Although the surface concentration of segregated hydrogen is low (\theta, usually 0.2–0.4 ML at T \text{\textasciitilde} T_m, depending on \theta_0), it is necessary to examine the region where the surface concentration of hydrogen is low enough to meet the requirement of Eq. (2). Fig. 4 shows the curves of ln(\theta) vs. 1/T plotted over a wide range of temperature. It can be seen from Eq. (1) that, if the surface concentration is too high, the second and third terms in Eq. (1) are not negligible and the curve of ln(\theta) vs. 1/T will no longer be a straight line. It can be seen from Fig. 4 that a linear relationship exists at temperatures above 260°C on Zr(10\overline{1}0) and 300°C on Zr(0001). Therefore the heats of segregation \Delta E, can be obtained from the slope of these two curves in the temperature range 260–380°C for Zr(10\overline{1}0) and 300–410°C for Zr(0001). The results are \Delta E = 10.1 kcal mol\textsuperscript{-1} on Zr(0001) and \Delta E = 10.7 kcal mol\textsuperscript{-1} on Zr(10\overline{1}0).

The heat of segregation is dependent on the release of elastic strain introduced by the dissolved segregant in the bulk, bonding with the free bonds of the substrate atoms on the surface and the formation of surface compounds. Hydrogen atoms dissolved in Zr prefer tetrahedral interstitial sites. The radius of these interstitial sites is about 0.0364 nm [12] which is close to the atomic radius of hydrogen (about 0.04 nm). Therefore the strain created by hydrogen dissolved in Zr is insignificant. The heat of hydrogen segregation is mainly due to the bonding between segregated hydrogen and Zr atoms on the surface or the formation of a surface Zr–H compound. If the heat of segregation is dominated by the bonding with the free Zr bonds at the surface, the free bonds at these two surfaces are different which will result in different heats of segregation. This is not the case here, and therefore it is possible that hydride-like products are formed on both surfaces giving similar heats of segregation. More information on the valence band structure is needed to understand the chemical state of segregated hydrogen, and this is presented in the next section.

3.2. The study of the binding of segregated hydrogen with surface zirconium atoms

The binding of segregated hydrogen atoms with surface zirconium atoms was investigated by monitoring the change in the valence-band-related AES transitions of Zr, such as ZrVVV and ZrMVV, during the segregation experiment.

Dillard et al. [18] have studied the formation of ZrH\textsubscript{x}, using X-ray photoelectron spectroscopy (XPS) and UPS during hydrogen exposure of a Zr surface at room temperature. They reported that about one-half of the surface Zr atoms form ZrH\textsubscript{1} on 100L exposure at room temperature and that this increases to more than 90% if the exposure is over 500L. An obvious change in ZrVVV and ZrMVV was observed when the Zr surface was exposed to 500L of hydrogen at room temperature [14]. The ZrVVV and ZrMVV Auger spectra of the Zr surface exposed to more than 500L of hydrogen were taken as a reference for surface hydride to permit a study of the formation of hydride on segregation. Fig. 5 shows the changes in ZrVVV and ZrMVV during annealing of the Zr(0001) sample at 120°C. For comparison, ZrVVV and ZrMVV spectra from a Zr surface exposed to 500L of hydrogen are also plotted. It is clear in Fig. 5
that the change in the valence band of Zr on segregation is towards that of a surface exposed to 500L of hydrogen. The spectrum of the surface exposed to 500L of hydrogen is not attained because the surface concentration of segregated hydrogen is lower than that for the 500L exposure, about 0.77 ML [13]. Therefore, we believe that the binding of segregated hydrogen with Zr is hydride like. It was found that, when the changes in AES (the growth of new peaks at 18.37 and 169.59 eV, the increase in peak height at 14.06 and 23.88 eV and the decrease in peak height at 8.87 eV) were plotted against the annealing time, all the changes were consistent with each other and exhibited the same trend. This may indicate that, as soon as segregated hydrogen atoms appear on the surface, the formation of hydride-like bonds occurs. A similar change was also observed on the Zr(1010) surface, which is consistent with the similar results on the heat of segregation.

The change in the surface dipole on hydrogen segregation was investigated by work function measurements. Unlike the other results, the work function changed in a different manner on the two surfaces. There was no detectable change in the work function on Zr(1010) during the segregation of hydrogen at various temperatures, which indicates that the location of segregated hydrogen may be in the surface plane. The work function also showed no change on adsorption of hydrogen on this surface, which may imply that the same locations are occupied by adsorbed and segregated hydrogens. In contrast, the work function increased when hydrogen segregation occurred on the Zr(0001) surface. Fig. 6 shows the changes in the work function, due to the segregation of hydrogen, on Zr(0001) during annealing at various temperatures. It has been reported by Tapping [19] that hydrogen atoms accept electrons when binding with zirconium atoms at the surface. Therefore the increase in the work function indicates that the location of segregated hydrogen atoms is outside the surface plane. When hydrogen was adsorbed on the Zr(0001) surface, the work function exhibited no detectably change at room temperature and increased to about 60 mV at −183°C when saturation was achieved (coverage of $6.9 \times 10^{14}$ atoms cm$^{-2}$). Fig. 7 shows the work function vs.
coverage during segregation at four temperatures. The contribution of each segregated hydrogen atom to the work function in the initial stage of segregation is linear with values of 871, 369, 166 and 20 mV/\(\times 10^{-15}\) atoms cm\(^{-2}\) at 150, 125, 100 and 75°C respectively. The linear relationship indicates that the segregated hydrogen atoms populate the same location as a function of coverage at each particular temperature with the same distance slightly out of the surface plane. The different contributions of each hydrogen atom to the work function at various temperatures indicate that hydrogen moves closer to the surface as the segregation temperature decreases.

3.3. The study of hydrogen diffusion

Since the segregation rate in the initial stages is controlled by the bulk diffusion of segregant atoms, the bulk diffusion parameters can be derived from the segregation rate in this region. In this work, systematic diffusion coefficient measurements were performed on both Zr(0001) and Zr(1010) surfaces.

3.3.1. An equation describing the relationship between bulk diffusion and surface segregation

A well-known equation describing the relationship between the bulk diffusion and surface segregation at a constant temperature was proposed by Mclean [20]. In the initial stage of segregation (\(D\varphi/\beta^2a^2\ll 1\)), this equation is as follows

\[
\varphi = 1 + 2r(\varphi) \beta^2a^2
\]

where \(r\) is the annealing time, \(\beta\) is the ratio of the segregated surface concentration to the bulk concentration of hydrogen and \(D\) is the diffusion coefficient. The diffusion coefficient can be obtained from the slope of the curve of \(\varphi \) vs. \(r^{1/2}\). This equation has been employed successfully to determine the bulk diffusion in many systems [11,21].

3.3.2. The determination of bulk diffusion coefficients along (0001) and (1010) directions

Fig. 8 shows the heating and cooling schedule used for diffusion measurements and the corresponding changes in the surface concentration of hydrogen during heating and cooling. It can be seen in Fig. 8 that the surface hydrogen atoms dissolve into the bulk completely when the temperature exceeds 500°C. After being held at 650°C for 2 min, the sample was rapidly cooled to one of a number of desired temperatures and held. A negligible amount of hydrogen atoms accumulated on the surface during the fast cooling to the lower temperatures. As soon as the desired temperature was reached and held, the hydrogen atoms started to segregate on the surface. Fig. 9 shows the curves of \(\varphi \) vs. \(r^{1/2}\) at six different temperatures on Zr(1010), illustrating the linear relationships. Similar experiments were also performed on the Zr(0001) surface. The bulk diffusion coefficients along (0001) and (1010) are shown in Table 1 and Fig. 10. The extrapolation of the results obtained by conventional methods on polycrystalline Zr at higher temperatures are also plotted for comparison.

The diffusion of hydrogen has been measured extensively in polycrystalline Zr by various methods [12]. However, no data are available for diffusion in a particular direction in a single crystal. It is shown in Fig. 10 that the diffusion of hydrogen in Zr is highly anisotropic: \(D = 0.173 \exp(-8807/RT) \text{ mm}^2 \text{ s}^{-1}\) in the (1010) direction, whereas \(D = 0.034 \exp(9565/RT) \text{ mm}^2 \text{ s}^{-1}\) in the (0001) direction. The difference is
Table 1

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<th>Temperature (°C)</th>
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<th>25°C</th>
<th>50°C</th>
<th>75°C</th>
<th>100°C</th>
<th>125°C</th>
<th>150°C</th>
<th>175°C</th>
<th>200°C</th>
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<td>(0001)</td>
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<td>0.596</td>
<td>0.920</td>
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<td>4.570</td>
<td>15.29</td>
<td>27.40</td>
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<td>(1010)</td>
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<td>0.817</td>
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<td>7.353</td>
<td>17.70</td>
<td>39.41</td>
<td>65.37</td>
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</tbody>
</table>

3.3.3. The effect of dissolved oxygen on the diffusion of hydrogen

An experiment was performed to investigate the influence of dissolved oxygen on hydrogen diffusion. The solubility of oxygen in zirconium is as high as 29%. The concentration of oxygen in the commercial Zr alloy was limited to less than several hundred parts per million. However, the oxygen concentration at some locations, such as underneath the oxide layers, will be much higher than the original amounts. An interesting question is whether this region (with high oxygen content) acts as a fast diffusion path for hydrogen. Due to technical difficulties, an understanding of the influence of a high oxygen content on the diffusion of hydrogen is not currently available. However, our segregation measurements provide an opportunity to investigate this important problem. From a previous study on the dissolution of oxide [23], it has been found that, after heating to a certain temperature, the oxide covering on the surface dissociates and oxygen atoms diffuse into the bulk. If the heating rate and temperature are controlled carefully, a high concentration of oxygen (about 10%–20%) in a region up to hundreds of angstroms below the surface can be obtained. The distribution of oxygen in the surface region (shown in the inset of Fig. 11) was obtained by forming an oxide, 12 Å thick, at ~830°C, followed by heating to 475°C and holding there for 5 min. After this procedure, the sample was cooled to a chosen

![Fig 10](image_url) Diffusion coefficients of hydrogen along the (0001) and (1010) directions and for a sample with a high oxygen content along the (1010) direction [8]. The broken line is an extrapolation of the published results at higher temperature for polycrystalline Zr.

![Fig 11](image_url) Comparison of the segregation rates on the Zr(1010) surface with and without a high content of oxygen near the surface.
temperature to let hydrogen segregation occur. The accumulation of hydrogen on this surface containing high amounts of subsurface oxygen occurred at a higher rate than on the clean surface (Fig. 11). The diffusion coefficients at four temperatures are shown in Fig. 10, which clearly indicates that the high oxygen content accelerates the mobility of hydrogen. Since the surface-segregated hydrogen atoms diffused from the bulk, passing through a non-uniform region (the concentration of oxygen changed from 20 to 100 ppm along the diffusion path of the hydrogen atoms), the diffusion coefficients in Fig. 10 are relevant to this particular condition. We cannot describe the quantitative effect of oxygen on the diffusion of hydrogen. However, it can be concluded that the presence of oxygen atoms promotes the mobility of hydrogen. The defects created by the high oxygen content may provide more pathways for hydrogen diffusion.

4. Conclusions

The segregation of hydrogen on Zr(0001) and Zr(1010) surfaces was studied by AES, work function measurements and SSIMS calibrated by NRA. It was found that hydrogen has a very strong tendency to segregate on these surfaces of Zr. The heats of segregation, measured by SSIMS which had been calibrated by NRA, were 10.1 and 10.7 kcal mol⁻¹ on Zr(0001) and Zr(1010) respectively. The valence-band-related AES transitions of Zr indicated that the modification of the Zr valence band by the segregation of hydrogen was very similar to that caused by surface hydride; this may contribute to the strong tendency for segregation to occur. The diffusion coefficients of hydrogen along the (0001) and (1010) directions in a single Zr crystal were measured by the kinetics of surface segregation. It was found that the diffusion along (0001), \( D = 0.034 \exp(-9565/R T) \) mm² s⁻¹, was slower than that along (1010), \( D = 0.173 \exp(-8887/R T) \) mm² s⁻¹. This may be explained by the different atomic densities on (0001) and (1010) faces, which affect the activation energy and partition function for diffusion. It was also found that the diffusion of hydrogen was enhanced by oxygen dissolved in zirconium.

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References


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APPENDIX V

The interaction of D₂O with Zr(0001) at 80 K

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Abstract

The adsorption of D₂O on Zr(0001) at 80 K and its subsequent reactions at higher temperatures have been studied by thermal desorption spectroscopy (TDS), work function measurements (Δφ), nuclear reaction analysis (NRA), low energy electron deflection (LEED), infrared reflection spectroscopy (FTIR-RAS), Auger electron spectroscopy (AES), and static secondary ion mass spectroscopy (SSIMS). D₂O adsorption on Zr(0001) at 80 K is accompanied by a ~1.33 eV. The adsorbed D₂O can be characterized into three layers by TDS: a chemisorbed layer (up to ~0.23 ML), an adsorbed layer, and an ice layer. The chemisorbed D₂O desorbed into OD₄ and D₄, and no desorption products could be detected, implying that the reaction products dissolved into the zirconium at temperatures appropriate for each component. The ice layer and most of the second adsorbed layer desorbed as molecular water during heating. The water adsorbed at 80 K did not form any long range ordered structure, but a (3 x 2) LEED pattern that was formed by heating the sample to temperatures above 430 K, is believed due to be an ordered oxygen superstructure.

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I. Introduction

Zirconium and its alloys are widely used in the nuclear industry for a number of reasons, including low neutron absorption cross section and excellent corrosion resistance [1]. The Zr-Nb alloys used in the Candu (Canada Deuterium Uranium) reactor afford improved creep resistance and strength. At high temperatures, hydrogen, either deliberately added or present as a result of radiolysis or corrosion reactions, may diffuse into the bulk of the alloy components, from where it can precipitate as hydride, possibly causing delayed hydride cracking (DHC). The desire for an improved understanding of the mechanisms of hydrogen ingress led to the present study of the interaction of D_2O with zirconium. This is also a very interesting system in its own right, since Zr is very reactive and can readily dissolve the possible reaction products, O and D.

Very few papers have been published in this area. Zeheringer et al. [2] studied the adsorption of water on polycrystalline Zr by photoemission experiments and found that the first adsorbed layer of water dissociated into adsorbed oxygen (O_w) and hydrogen (H_w) and/or (OH)_w and H_w at 100 K. This experiment was really only a reference study for research on the adsorption of water on amorphous Ni_wZr_w. To the authors' knowledge, no other well controlled studies on water-zirconium system have been published.

We report here studies of the interaction of water with Zr(0001) at 80 K, using TDS (thermal desorption spectroscopy), Δϕ (work function change), NRA (nuclear reaction analysis), LEED (low energy electron deflection), FTIR-RAS (Fourier transform infrared-reflection absorption spectroscopy), AES (Auger electron spectroscopy) and SSIMS (static secondary ion mass spectroscopy).

II. Experimental

The experiments were performed in two separate stainless-steel ultrahigh vacuum chambers. The FTIR-RAS, Δϕ, LEED, and TDS experiments were carried out in a chamber pumped by a turbo-molecular pump backed by a diffusion pump, and which operates in the low 10^-10 torr range. D_2O was dosed onto the sample using a shuttered, differentially pumped capillary array which is described in more detail elsewhere [3].

The second chamber equipped for AES, SIMS, NRA, LEED, and Δϕ was pumped by trapped diffusion and Ti-sublimation pumps allowing base pressures of < 5 x 10^-11 torr to be achieved. This chamber is interfaced to a 2.5 MV van de Graaff accelerator via a differential pumping bench.

Two methods were used to dose D_2O in the second chamber. One used a capillary doser similar to that in the first chamber, the other involved raising the ambient pressure to ~ 1 x 10^-6 torr. Work function measurements were used to inter-calibrate the dosing rate and total fluence in the two chambers and the two dosing methods in the second chamber. A detailed description of the second chamber can be found in refs. [4 - 6].

The elliptical single crystal sample (12 mm x 8 mm x 1.5 mm) was cut from a 99.99% pure zirconium single crystal rod of 3 mm diameter provided by Chalk River Laboratories, and oriented and polished to within ± 0.5° of the basal plane ((0001)). Two 2 mm wide nickel ribbons were spot welded to the back of the crystal and suspended between two posts that were normally cooled to liquid nitrogen temperature. A K-type thermocouple was spot welded to one edge of the sample, and a temperature controller could provide linear temperature ramps or hold the crystal temperature to ± 0.5 K by resistive heating. The sample was first bombarded by 1 keV Ar⁺ ions at a current density of about 3 μA cm⁻² for 2 hour to remove the original oxide layer and other contaminants (C, Cl, and F). The heating-cooling-sputtering cycles were designed to remove the bulk impurities such as Si, Cl, Fe, Ni, and H. The sample was annealed at 920 K for 2 min to dissolve the residual oxygen on the surface before each experiment. A sharp (1 x 1) LEED pattern was observed.

III. Results and discussion

3.1 NRA determination of coverage

NRA was employed to determine the absolute coverage of D_2O on Zr(0001) at different exposure at 80 K. Two dosing methods were used in this measurement. The first method used a shuttered, differentially pumped capillary array. In order to compare the NRA results to other measurements (TDS, AES, etc.) in the same chamber or measurements in the other chamber, a calibration of Δϕ versus coverage is required. Second, for convenience it is desirable to determine the flux from the capillary doser. First NRA was used to measure the coverage produced by the capillary doser under standard conditions (present pressure in the doser source) for a chosen exposure in seconds. The coverage attained in 100 s by backfilling the chamber to 1 x 10^-6 torr D_2O, (which produces a 1 Langmuir exposure, 1 L, where 1 L = 1 x 10^6 torr-s) was also measured. By comparing the absolute coverage produced by this method to that from the capillary array doser, the localized D_2O pressure at the Zr(0001) achieved using the capillary doser can be determined. (Note: although the calibration factor for our gauges for D_2O is unknown, this does not affect either the absolute coverages or their intercomparison which is achieved by Δϕ measurements).

Fig. 1 shows the NRA results achieved using the capillary doser. Two nuclear reactions were used: the ³He(⁴He, p)⁴He
reaction, by which the absolute coverage of deuterium can be determined and the \(^{18}O(\text{'H, p})^{16}O\) reaction, by which the absolute coverage of oxygen can be determined. The absolute coverage of D\(_2\)O should be the same as oxygen coverage, but half of the deuterium coverage (measured as D, not D\(_2\)) provided no selective desorption of O or D occurs. Many oxygen related experiments have been performed on this crystal, resulting in a high \(^{18}O\) background signal. Provided that no deuterium is lost during adsorption at 80 K, (none was detected by mass spectroscopy during the dosing), we believe that the D\(_2\)O coverage is more reliably determined via the deuterium coverage. Certainly the statistical error limits are much smaller for the D-measurements as shown in Fig.1. The absolute coverage of water should be equal to half of the D-coverage, as shown as the dashed line in Fig. 1. The agreement is within the combined uncertainties of the experimental data, and lends support to the observation that no deuterium is lost from the surface during dosing at 80 K. By comparing the dosing rates using the capillary and background dosing methods, we established that: i) 1 sec capillary dosing produced 0.0052 ML of D on Zr(0001); ii) background dosing produced a D-coverage of 0.90 ML (1 ML = 1 monolayer = \(1.11 \times 10^{15}\) D cm\(^{-2}\)) for an apparent exposure of 1 L D\(_2\)O. Fig. 1 shows that 200 seconds of capillary dosing produces 1.04 ML of D, which is equivalent to 1.04x0.90 = 1.16 L of exposure. The local pressure at the sample while using capillary dosing is thus \(1.16 \times 10^6\) torr. When corrected for background pressure, the local water pressure at the sample is about 5.3 x 10^6 torr for these conditions which could be readily reproduced. This result was confirmed by comparing \(\Delta P\) during D\(_2\)O exposure using the capillary dosing, with that produced by raising the ambient pressure to 5.8 x 10^6 torr.

The NRA results make it possible to convert the capillary dosing time not only to the absolute water coverage (1 sec capillary dose = 0.0026 ML of D\(_2\)O) but also the exposure in Langmuir units (1 L = 0.45 ML of D\(_2\)O), as shown in the top x-axis in Fig. 1.

The effect of heating on the absolute coverage of D was determined as follows. First, 0.78 ML D\(_2\)O were adsorbed on the surface at 80 K, the sample was then heated to a chosen temperature and cooled back to 80 K. Then the absolute coverage of the residual deuterium was measured by NRA. Fig. 2 shows the results (shown as the D coverage divided by a factor of 2:0; this equals the total D\(_2\)O coverage if there is no desorption) obtained after annealing the sample to 240 K, 300 K, 400 K, and 600 K respectively. A large decrease in absolute D-coverage occurs between 80 K and 240 K. The D-coverage then stays constant from 240 K and 300 K, at about 0.46 ML of D (plotted as 0.23 ML of deuterium), decreases by ~0.06 ML D by 400 K, and decreases to zero by 600 K. We will discuss this together with the TDS results in the next section.

3.2 TDS characterization of D\(_2\)O adsorption
3.2.1 Adsorption at 80 K

Fig.3 shows the thermal desorption spectra of mass 20 (D\(_2\)O) after different D\(_2\)O exposures at 80 K. No D\(_2\)O desorption was found when the D\(_2\)O exposure was less than 90 seconds which produces a coverage of ~0.23 ML. We term the adsorbed layer formed below the
critical exposure of \( \sim 90 \) s the "chemisorbed layer". At D_2O exposures greater than or equal to 90 seconds, a thermal desorption peak occurs at 178 K which increased in intensity with increasing D_2O exposure. A second peak, centered at 163 K, was first detected as a shoulder on the first peak, when the D_2O exposure was greater than 200 seconds. With further exposure, the intensity of the 163 K peak increased steadily without saturation, while the 178 K peak tended to saturation. Given that no water desorption can be detected for exposure of \(< 90\) s, and that the 178 K peak can be saturated, we attribute it to desorption of D_2O from a second adsorbed layer; the 163 K peak then arises from an ice layer. We do not intend this terminology to indicate completion of the chemisorbed layer at coverages of only \( \sim 0.2 \) ML (Fig. 3a) but rather that the onset of water desorption which we describe as arising form the second layer, indicates a change in reactivity of the adsorbed water. This second layer might well be chemisorbed, albeit relatively weakly. The question of whether the water dissociates upon adsorption up to coverages of \( \sim 0.2 \) ML is addressed later (Section 3.4). The desorption peak temperature of the second adsorbed layer is independent of the initial coverage indicating that the desorption of D_2O follows first order kinetics. Using the peak temperature of this second adsorbed layer (178 K) we can estimate the first-order desorption energy to be 54.9 kJ/mol, assuming a pre-exponential of \( 10^{15} \) s\(^{-1}\). The change in intensity of the second layer and the "ice" peaks at different initial D_2O coverages, are plotted in Fig. 4. It can be seen in this plot that the desorption of the second adsorbed layer D_2O starts at 90 seconds exposure and saturates at one 260 second exposure at which point the surface has \( \sim 0.23 \) ML chemisorbed water, 0.31 ML second layer and 0.14 ML ice. The ice layer desorption starts at 200 seconds and increases rapidly, eventually becoming linear with exposure. This state exhibited zero order desorption kinetics.

Fig. 3 shows the desorption of deuterium during heating after D_2O exposures at 80 K. There are several D_2 desorption peaks at high D_2O exposures, but no D_2 desorption was found when the D_2O coverage was smaller than \( \sim 0.20 \) to 0.23 ML. This is consistent with the data in Fig. 3a which shows that the chemisorbed (reactive) water layer is completed by this coverage. The low temperature D_2 peaks accompany the desorption of D_2O, and originate from the decomposition of D_2O in the mass spectrometer. The D_2 peak centered above 300 K did not appear until coverages \( \sim 0.23 \) ML, at which the second adsorbed layer began to fill. The intensity of this D_2 peak against exposure is shown in Fig. 4 in which the TD data for the second and ice layers are also shown. The intensities of the high T D_2 and the second layer peaks saturate at about the same exposure, indicating that the D_2 desorption occurring at T > 300 K originates from the second adsorbed layer of adsorbed D_2O. The implication is that the second adsorbed layer of D_2O did not completely desorb as molecular water at 178 K, but that a small amount dissociated at a higher temperature, eventually yielding the desorption of molecular deuterium and leaving behind adsorbed oxygen in an undetermined chemical state. The interpretation of the data in Fig. 2 is now clear.
The decrease in coverage (determined via the areal density of D-atoms) which occurs upon heating the sample from 80 K to 240 K on Zr(0001) with 0.78 ML of pre-absorbed D₂O, must be due to the desorption of the second layer and ice layer of water. The small decrease in deuterium coverage of about 0.06 ML D from 300 K to 400 K, is related to the D₂ desorption peak at about 320 K. Presumably this indicates that of the 0.31 ML D₂O in the second adsorbed layer, ~ 0.28 ML desorb molecularly and 0.03 ML desorb as D₂.

3.2.2 Adsorption at 158 K

Exposure of the Zr(0001) surface to D₂O at 158 K, prevents formation of the ice layer because the temperature is above the desorption temperature of the ice layer. The second layer will still be populated because the temperature is below its desorption temperature. This permits the study of the properties of the chemisorbed and second adsorbed layer. Fig. 5 shows the TD and Δφ data for an experiment in which the Zr(0001) sample was exposed to D₂O for 360 s at 158 K, cooled to 80 K, then heated to permit measurements of the desorption behavior. We estimate the coverages of chemisorbed water and second layer water at 0.23 and 0.37 ML respectively. Desorption is thereby detected from only the second adsorbed layer (173 K) together with the D₂ desorption peak at about 330 K. The area of the 173 K peak versus exposure is the close to that for the second adsorbed layer shown in Fig. 4. Also show in Fig. 5 are Δφ data obtained during desorption. Note the small decrease in Δφ accompanying the desorption of molecular water below 200 K, and the very large increase that overlaps into the region of molecular deuterium desorption.

3.3 Work function change (Δφ)

Fig. 6 shows the variation of Δφ of the Zr(0001) surface as a function of exposure (capillary array) to water at 80 K. Δφ was found to decrease with D₂O exposure, eventually saturating at ~ 1.33 eV. Our TDS data indicate that the adsorption process can be divided into three regions according to the exposure: 1) chemisorbed layer, which occurs during the first 90 s (or 0.23 ML, or 0.52 L); 2) second adsorbed layer, which starts at 90 s and saturates at 260 s (or 0.67 ML, or 1.5 L); 3) ice layer, which starts to build up at 200 s (or 0.51 ML, or 1.14 L) and of course never saturates. The 0.23

Fig. 6 The change of work function (Δφ) with D₂O exposure on Zr(0001) at 80 K. The absolute D₂O coverage at different exposure is also plotted. The label on the top of the graph indicates the adsorption stages defined by the thermal desorption experiments.
ML of chemisorbed water is accompanied by a $\Delta \phi$ of - 1.06 eV (80% of the total change). The work function continues to decrease with the formation of the second adsorbed layer, but is almost saturated by the point at which the second layer is completed.

Fig. 7 illustrates the change in work function that occurs on heating the sample with 0.42 ML D$_2$O pre-adsorbed at 80 K (160 s capillary dosing). The work function starts to increase at $T \approx 190$ K, where the desorption of the second and ice layers is just completed. There is no sign of the decrease in $\Delta \phi$ at low $T$ observed for the higher starting coverage in Fig. 5. $\Delta \phi$ increases continuously up to 362 K, and then decreases to a minimum value at 593 K before then increasing again to a plateau at $T > 750$ K a temperature at which all products of reaction should have dissolved or desorbed.

3.4 FTIR-RAS

Infrared reflection spectra for Zr(0001) exposed to D$_2$O at 80 K are illustrated in Fig. 8. At the lowest coverages (below 90 s exposure, or < 0.32 L) when only the chemisorbed state is populated, a single absorbance feature is observed which is associated with an OD stretch at 2670 cm$^{-1}$. There is no evidence for molecular water clusters which are characterized by an D-bonded band at 2543 cm$^{-1}$ and a higher frequency peak which originates from non-H-bonded OD groups at the outside of the clusters. The position of the OD stretch which is observed is different from either of these features, although we do not know the expected absorption frequencies for an isolated D$_2$O molecule. The absence of an IR signature for D$_2$O could originate form at least two causes. The first

Fig. 8 The FTIR-RAS spectra of Zr(0001) surface after different D$_2$O coverages. Curves 1, 2, 3, 4, 5, and 6 correspond to the 0.052 ML, 0.156 ML, 0.234 ML, 0.312 ML, 0.52 ML, and 0.78 ML of coverage respectively. The absorption peak for the D$_2$O stretch in ice is at 2543 cm$^{-1}$. OD stretches are visible at 2670 cm$^{-1}$ and 2732 cm$^{-1}$.

Fig. 9 The FTIR-RAS spectra of Zr(0001) surface after adsorption of 0.16 ML of D$_2$O at 80 K, followed by heating to indicated temperature, and cooling to 80 K. The inset shows the area of the OD absorbance peak remaining after the brief heating to the indicated temperatures.
is that there is no molecular D$_2$O on Zr(0001) surface at low coverage (< 0.2 ML); the second is that the dipole of the adsorbed molecular D$_2$O is parallel to the Zr(0001) surface and that the surface selection rule is responsible for the absence of IR absorption. Our TDS data unequivocally point to dissociation of the water molecules at elevated temperatures, and the absence of any desorption for coverages below about 0.2 ML is circumstantial evidence for dissociation at still lower temperatures. Fig. 9 illustrates the results of IR spectra taken to determine the nature of the OD species under conditions that dissociation is known to occur. The sample was exposed to about 0.35 ML of D$_2$O at 80 K, warmed to the indicated temperature for a few seconds, and then recooled to 80 K; the IR absorption spectra then being acquired at 80 K. It is clear that the OD stretch does not shift in frequency, the implication being that dissociation must be occurring at the adsorption temperature of 80 K. The insert in Fig. 9 shows the area of the OD absorbance peak as a function of the different annealing temperatures. The intensity of the OD stretch does not increase as the temperature is increased from 80 K, rather it decreases at $T \geq 250$ K, disappearing entirely by $\sim 370$ K. These data imply i) that all the D$_2$O adsorbed after 0.35 L exposure at 80 K, (\sim 0.14 ML) dissociates upon adsorption and that the OD groups so formed are stable at $T \geq 250$ K, and dissociate further between 250 and 350 K although no D$_2$ desorption was detected because the D$_2$O diffuses into the bulk (see section 3.5) This latter temperature region is however the one in which D$_2$ desorption is detected (Fig. 3b) for higher starting coverages.

At higher exposures (coverages above 0.3 ML; Fig. 8) we expected hydrogen bonded OD stretch band is detected at 2543 cm$^{-1}$ (corresponding to clusters of D$_2$O) together with another peak at 2732 cm$^{-1}$ which is the non hydrogen-bonded OD stretch at the edge of molecular D$_2$O islands. The peak we have associated with adsorbed OD from dissociated water (which we will now term OD$_{ad}$) is still visible at 2670 cm$^{-1}$, although it is barely detectable in the spectrum at 0.78 ML and might be less intense by 0.52 ML. The correlation between the data in Figs. 3a and 8 clearly indicate that the second adsorbed layer must consist mostly of molecular water. The existence of the OD$_{ad}$ from dissociated water and molecular water is interesting and suggests phase separation since the apparent decrease in the intensity form the OD$_{ad}$ species at high coverage might be due to D-bonding with molecular water, shifting its frequency into the 2543 cm$^{-1}$ bond. The observation that D$_2$ desorption was now detected indicates that the additional D resulting from the dissociation is a small fraction of the second adsorbed layer, must somehow be prevented from diffusion into the bulk of the Zr.

3.5 Time, temperature and coverage resolved AES and SSIMS

3.5.1 Time dependence

In this section we report static SIMS (SSIMS) and Auger spectroscopic measurements of surface species produced during the interaction of D$_2$O with Zr(0001). Adsorption was carried out at 80 K. The SSIMS measurements utilized a current density of $4 \times 10^4$ A/cm$^2$ during the entire measurement; this means that on average only 0.1 % of the zirconium atom on the surface are hit by a primary ion. Previous measurements using SSIMS to measure deuterium uptake proved that neither the adsorption process nor the adsorbed layer are affected by fluences of this magnitude [8]; Fig. 10 shows the results of this experiment. The OD uptake first follows a linear relation with coverage up to 0.23 ML, then increases at a slightly faster (but linear) rate up to a coverage of ~0.6 ML, before gradually slowing. This behavior is understandable if we refer to Fig.6. The first linear part corresponds to the adsorption of the chemisorbed layer for exposures resulting in coverages ≤ 0.23 ML.
At higher exposures, the second adsorbed layer forms (chemisorption might still be occurring on uncovered areas of the surface). The increase in rate is probably due to a change in the SIMS yield of this ion which now arises from a molecular species. (At 80 K the sticking coefficient for water is probably 1.0 and constant with coverage). The decrease in the slope of ion yield versus coverage above ~0.63 ML is understandable as the second layer becomes saturated and the entire adsorbed layer asymptotically approaches a condition in which the adsorption of an additional water molecule changes only the thickness of the layer, the ion yield no longer being affected by proximity to the metal surface. A similar approach towards a constant yield can also be seen in $^{12}$C and $^3$H uptake curves.

The yields of the ZrO and ZrO$_2$ ions were also monitored (Fig. 10b) to gain insight into the oxidation of the Zr substrate (Fig. 10b). Our previous studies of oxidation of Zr by O$_2$ have shown that the ZrO$^-$ ion is characteristic of adsorbed O or Ar with dissolved oxygen and the ZrO$_2$ ion increases in magnitude as ZrO is formed[9]. The ZrO$^-$ ion appears at the lowest exposures and exhibits a similar behavior with respect to coverage as the O$_2$ ion. ZrO$_2$ first appears at just above 0.1 ML, tracks the ZrO$^-$ ion and then increases linearly (and more rapidly than any other ion species) above 0.8 ML.

Fig. 11 shows the AES data under the same conditions as Fig. 10, for the O(KLL), Zr(MNN) and Zr(MNV) transitions. The MNV transition is sensitive to the oxidation state of the Zr surface since the Zr(MNV) transition shifts from 147 to 140 eV when Zr$^+$ is oxidized to Zr$^{2+}$. This makes it possible to study the formation of oxide by monitoring the change of the Zr(MNN) peak. The MNN transition provides information on the Auger yield from the surface that to a first approximation should only be affected by (eg) scattering in an overlayer containing fewer Zr atoms cm$^{-2}$. The O(KLL) peak increased nearly linearly with O$_2$ coverage up to ~0.6 ML. By comparing the O(KLL) differential peak-to-peak height to the absolute coverage determined by NRA at the same D$_2$O exposure, the intensity of the O(KLL) peak can be calibrated to the absolute amount of oxygen. Following our previous practice, we actually used the O(KLL)/Zr(MNN) ratio rather than the O(KLL) intensity to compensate for fluctuations in the experiments. Fig. 12a illustrates the excellent linear relationship between the absolute coverage and the O(KLL)/Zr(MNN) ratio. The slope was found to be 0.722, this is very close to the result obtained from similar experiment: of oxygen uptake (0.738) resulting from exposure to O$_2$ [7]. Fig. 12b shows the resulting calibration of absolute coverage versus D$_2$O exposure. It can been seen that the D$_2$O uptake on Zr(0001) at 80 K follows a linear relationship; number of ML = 0.44 times the exposure in L. The Auger data for the MNV transition also indicates the

Fig. 11 The change of AES peak-to-peak height for the O(KLL), Zr(MNN), Zr(MNV)$_{000}$ and Zr(MNV)$_{001}$ transitions during the D$_2$O adsorption on Zr(0001) at 80 K.

Fig. 12 a) Comparison of the O(KLL)/Zr(MNN) ratio to the absolute coverage of oxygen determined by NRA; b) Oxygen uptake kinetics during exposure of Zr(0001) to D$_2$O at 80 K, determined by calibration of the O(KLL)/Zr(MNN) ratio by NRA.
formation of oxide at coverage above ~0.8 ML. This is similar to the observations made in earlier studies of the reaction of Zr(0001) with O₂ [7]. The coverage at which the Auger data show formation of oxide correlates with the point at which the SSIMS results show an accelerating rate of formation of the ZrO₂ ion (Fig. 10b). The formation of this ion at lower coverages cannot thus be taken as a signal of oxide formation. Because adsorbed water is sensitive to electron beam induced dissociation, we cannot make more definitive statements, but the results did not appear to be electron-beam-fluence dependent under the conditions of our experiments.

3.5.2 Temperature dependence

A comparison of the TD data and in situ analytical data (SSIMS, AES) can provide information of the mechanisms by which species are removed from the surface. Since both O and D readily dissolve in Zr [4 - 9], this must be considered in any analysis. Fig. 13 shows the SSIMS data for a sample preexposed to D₂O at 80 K to a coverage of 0.9 ML, and then heated. All 3 adsorbed species would be present: chemisorbed, second layer and ice layer. Fig. 13b shows that the D₂O ion disappears below 200 K, the temperature by which all desorption of molecular water is completed. By contrast, the OD⁻ ion yield decreased steadily at the very beginning of the heating, was then constant to ~130 K and decreased rather monotonically through the molecular desorption region, disappearing by ~450 K. It therefore continued to decrease even in the region between ~200 and 270 K in which no desorption was detected (Fig. 3b). Our previous studies have indicated that oxygen and hydrogen do not rapidly diffuse into Zr at temperatures below ~500 K and so the steady disappearance of the OD⁻ ion below this temperature cannot be attributed to dissolution or desorption, but must originate from dissociation and/or changes in ion yields per incident Cs⁺ ion. We emphasize that the Cs⁺ ion flux was far too low to cause significant disturbance of the adsorbate layer(s). The disappearance of the OD⁻ ion should be correlated with the infrared results illustrated in Fig. 9. While both data sets therefore support the idea that the OD bond is being broken by reaction with the Zr surface, between ~250 and 350 K, the decrease in the OD⁻ SIMS yield below 250 K must also be partly attributable to loss of molecular water and possibly, changes in ion yields. In this regard the data in Fig. 7 are very interesting. The work function of the surface at ~220 K, after desorption of molecular water from the ice and second layers, is still ~1.2 to 1.3 eV below the clean surface value. It then increases by ~1 eV between ~240 and 340 K. Very little desorption occurs in the lower temperature part of this region, and desorption of D usually produces only a very small change in Δφ [10], so this large increase cannot be attributed to desorption. The OD⁻ SIMS yields decrease rapidly in this region as does the IR intensity of the OD stretch attributed to ODₐ in so the ~1 eV increase in Δφ must be due to decomposition of ODₐ into O amazon and Dₐ implying a large negative dipole for the ODₐ species.

The O⁻ yield also first rapidly decreases and then stays constant to ~140-150 K and drops to a plateau after the completion of desorption of molecular water, before decreasing again at ~240-500 K, disappearing entirely by 800 K. The decrease in intensity below between ~140 and 200 K is related to the desorption of the second adsorbed and ice D₂O layers. The origin of the initial rapid decrease is unknown but is most likely an artifact of the SIMS measurements as the experimental parameters stabilize. Comparison of the SSIMS yields with O(KLL) data (not shown) indicate that the O⁻ yield starts to decrease at low temperatures (~450 K) than the O(KLL) intensity (~600 K). This almost certainly reflects the different surface specificities of SSIMS and AES. Since we know that O moves to subsurface sites at elevated temperatures, this would result in a much larger decrease in SIMS yields compared to the O(KLL) Auger intensity. The D⁻ yield drops to zero by ~600 K and does not appear to specifically reflect the molecular desorption seen in TD data although there might be a slight increase above about 300 K. NRA data indicate that this is a minor loss mechanism anyway (Fig. 2). Fig. 13b also illustrates the SSIMS yields for the ZrO₂ and ZrO⁻ ions which decrease monotonically with

Fig. 13 SSIMS on Zr(0001) with 0.9 ML D₂O preadsorbed at 80 K, as a function of temperature.
temperature, the latter ion disappearing first (at lower temperature) as would be expected since the oxide will decompose first to produce dissolved O and a stoichiometry far from ZrO$_2$.

3.6 LEED

The Zr(0001) surface gave a sharp (1 x 1) hexagonal LEED pattern. No new fractional order pattern was formed upon adsorption of water, but the diffused background intensity increased. However, if the sample was heated after water exposure, then a LEED pattern with apparent 2 x 2 symmetry could be produced. Fig. 14 shows such a sequence. Fig. 14a shows the LEED pattern of the clean surface, 14b the same surface after adsorption of 0.25 ML D$_2$O at 80 K, followed by heating to 450 K, and cooling to 80 K for acquisition of the LEED data. Our other data indicates that there are no OD groups on the surface at 450 K and perhaps 0.1 to 0.2 ML D (Fig. 2), plus chemisorbed O. Detailed LEED studies (11) have indicated that the 2 x 2 pattern associated with 0.5 ML O produced by exposure of Zr(0001) to O$_2$, followed by annealing, usually arises from 2 x 2 domains (each 0.25 ML) situated between the first and second Zr layers, and the second and third Zr layers. The diffraction pattern observed in the present study could then arise from either a single domain of 2 x 2-O (0.25ML) or from 2 domains of 2 x 2-O (each with less than the ideal coverage of 0.25 ML, but summing to 0.25 ML) spread between the first and second, and the second and third Zr planes. The intensity of this ordered LEED pattern increased with the D$_2$O coverage up to ~ 0.25 ML, the coverage below which only the chemisorbed layer was formed. At coverages above 0.25 ML, the fractional order spots elongate in the three symmetry directions rotated 120° to each other. (This is similar to what happened in O$_2$ uptake, but at coverages above 0.5 ML. If these higher exposure surfaces are annealed to 550 K, the elongated spots becomes sharp again and even more intense that the pattern at the lower coverage.

As mentioned above, the maximum in the half-order intensities for the superstructure produced from oxygen adsorption and annealing occurs at 0.5 ML and recent dynamical LEED analysis unequivocally indicated the presence of two, 2 x 2, 0.25 ML O-domains between the surface lattice planes (11). The present observations suggest that with water as the adsorbate, it is possible to produce ordered 0.25 ML 2 x 2 domains in a single atomic plane. Further, the streaking observed between 0.25 and ~ 0.5 ML of presorbed D$_2$O indicates saturation of these sites at lower coverages than observed with oxygen as adsorbate where streaking occurs at coverages well above 0.5 ML. As the total oxygen coverage reaches ~ 0.25 ML, annealing to 550 K results in the desorption or dissolution of all the D, the oxygen atoms can arrange themselves into the most stable arrangement, a single 2 x 2-O domain between the first and second atomic planes of the Zr(0001) substrate. It appears that the formation of the structures must be kinetically limited and perhaps the residual ad(ab)sorbed D plays a role in preventing the diffusion of O into the deeper subsurface sites between the second and third layers.

With the further increase of the D$_2$O exposure and coverage above 0.5 ML, a new LEED pattern emerges, shown in Fig.15. This is the LEED pattern of the Zr(0001) surface after dosing D$_2$O to a coverage of 0.6 ML, followed by annealing to 623 K for 30 seconds. In this case, no fractional order spots appeared until this annealing temperature is reached. The observed pattern appears to be a combination of (2 x 2) and (-3 x -3) patterns. Presumably this pattern could arise from coexistence of (2 x 2) and (-3 x -3) domains at coverages between 0.25 and 0.33 ML. Such a structure cannot be formed by oxygen exposure and annealing and again indicates kinetic control over the structures.

Fig. 14 LEED pattern of Zr(0001) surface after annealing the sample at 450 K for 30 s.

a) the clean surface; b) after 40 s D$_2$O adsorption at 80 K; c) after 120 s D$_2$O adsorption at 80 K; d) further annealing at 550 K for 30 seconds after c).

Fig. 15 LEED pattern of Zr(0001) after 240 s D$_2$O exposure at 80 K followed by annealing at 623 K for 30 s.
IV Conclusions

1) The adsorption of $D_2O$ at 80 K can be divided into three stages: a chemisorbed layer (coverages between 0 and $-0.25$ ML), second adsorbed layer, up to a total coverage of $-0.65$ ML, and an ice layer. The $D_2O$ in the chemisorbed layer is probably all dissociated into $OD_{ad}$ and $D_{ad}$ although we cannot eliminate the possibility of some further dissociation into $O_{ad}$ and $D_{ad}$.

The second adsorbed layer is molecular water and begins to form before the chemisorbed layer is fully saturated. Molecular water can desorb from this layer at 173 K. The ice layer begins to form before the second adsorbed layer is fully covered, and desorbs with zero order kinetics at 163 K. Most of the water in the second adsorbed layer desorbs molecularly from about 175 K, but some (~10 to 20%) dissociates between 200 and 300 K to form either $O_{ad}$ and $D_{ad}$ or $OD_{ad}$ and $L_{ad}$ or a combination of all three components. The $OD_{ad}$ species dissociate above ~240 K, and $D_2$ desorbs above 300 K. The observation of the desorption of $D_2$ is unusual, as with a "pure" $D_{ad}$ layer, all the $D$ dissolves into the bulk of the Zr sample [10]. This could indicate that the $O_{ad}$ present on/in the surface, prevents the dissolution of $D$. This mechanism is unlikely since we have observed that adsorbed $O$ actually reduces the barrier to dissolution of hydrogen [8]. An alternative explanation of the disappearance of $OD$ and desorption of $D_2$ is the following reaction:

$$-OD_{ad} + -OD_{ad} = O_{ad} + D_2(g)$$

2) The work function decreases linearly with the coverage of the chemisorbed layer. The magnitude of the decrease ($~1.0$ eV) is similar to that expected from molecularly adsorbed water, but in this case arises from the dissociation products. Sequential adsorption of $O$ and $D$ would not produce a similar change in work function and so the $\Delta \phi$ is probably mostly associated with the $OD_{ad}$. The breaking of the this O-D bond is associated with a large increase in $\Delta \phi$. Further heating above 400 K causes a slight decrease which we associate with O moving to subsurface sites and formation of the ordered superstructure and finally the dissolution of $O$ above ~600 K (increasing $\Delta \phi$ towards the clean surface value).

3) There is evidence of the formation of oxide at the highest coverages, but this could be an Auger beam artifact.

4) Adsorption of $D_2O$ at 80 K does not result in the formation of any new LEED superstructure. A (2 x 2) LEED pattern was observed upon annealing 0.25 to 0.5 ML coverages of adsorbed water above 450 K. The pattern probably originates from $O$ incorporated between the first and second Zr layers. A new ($\sqrt{3} x \sqrt{3}$) LEED pattern was formed that coexisted with the 2 x 2 phase was formed at higher initial water coverages, followed by annealing above 600 K.
References


