The interaction of H_2O molecules with iron films studied with MIES, UPS and XPS

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ABSTRACT

X-Ray Photoelectron Spectroscopy (XPS), Metastable Induced Electron Spectroscopy (MIES) and Ultraviolet Photoelectron Spectroscopy (UPS) were applied to study the interaction of H_2O molecules with iron films. During the interaction with H_2O molecules under ultrahigh vacuum conditions, an oxide film is formed on the iron surface. UPS and XPS still show metallic contributions, even for a surface which is exposed to about 10^3 L. The oxide film thickness amounts to about 1.8 nm. No hydroxide formation is observed at all, neither in UPS nor in MIES. Further impinging H_2O molecules do not interact with the surface, because the oxide film inhibits the dissociation of impinging molecules.

H_2O exposure beyond 10^9 L does not lead to a significant increase of the oxide layer, which saturates at a thickness of 1.8 nm. In particular, no surface hydroxide is observed at this exposure. Neither XPS UPS nor MIES reveal any indication for this.

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1. Introduction

Iron is known to be very corroding under ambient conditions. Complex electrochemical models have been employed to explain the corrosion and the corrosion pathways (see for example [1,2]). Iron is reported to be very reactive against SO_2, HCl and moderate reactive against O_2, H_2O, CO_2 and organic acids like HCOOH. Following the macroscopic picture the formation of rust layers is a three step process [1]:

1. Formation of a thin oxide/hydroxide layer with a thickness between 1 nm and 4 nm within several milliseconds. This film is found to be stable and passivating in the absence of atmospheric impurities as well as in the absence of relative humidities beyond 60%.
2. In aqueous environments (humidities beyond 60%) this oxide/hydroxide layer changes into one of two types of green rust $(Fe_2O_x(OH)_y)$ or $(Fe_3O_x(OH)_y)$, which both consists of Fe^{2+} und Fe^{3+} within several hours.
3. Transformation into the fragile brown rust consisting of iron oxides and hydroxides $(Fe^{3+}$ only) subsequently.

Following literature these macroscopically described processes only require an aqueous atmosphere with a humidity of at least 60%.

Another couple of recent publications deal with the reaction of water with iron [3–6]. A common observation is the growth of a passivating oxide layer. The adsorption of large amounts of OH groups is only detected at high water exposures $(>10^4$ L) [3]. The proposed model of Grosvenor et al. for the rate-limiting step is the generation of hydrogen atoms because of the H_2O dissociation at the surface. These can either hinder the diffusion in the oxide layer or block vacant surface sites and thus hinder a further dissociation [3]. Another suggestion by [4] is the formation of Fe^{3+} cations which might also have an influence on the adsorption onto and on the diffusion into the surface layer. The adsorbed OH groups are not incorporated into the lattice but chemisorbed on top of the iron oxide layer which is shown by Angular-Resolved Photoelectron Spectroscopy (ARPES) measurements [3].

A publication by Roberts and Wood deals with the investigation of the interaction of water vapor with iron surfaces applying X-ray Photoelectron Spectroscopy (XPS) [7]. They expose iron surfaces to a variable water partial pressure of 10^{-7} to 10^{-1} torr. Their work supports the macroscopic view, e. g. proposing a passivating iron oxide layer with a maximum thickness of 20 Å. We will show in this publication that we can confirm these results, but we can moreover provide additional information on the processes happening on the topmost surface layer of an iron film applying Metastable Induced Electron Spectroscopy (MIES).

This method has been applied before for the interaction of oxygen molecules with the iron surface by our group [8]. We found that even an oxygen saturated surface shows a metallic Fe contribution in XPS. The dissociation of oxygen molecules is hindered as soon as a certain coverage with iron oxide is achieved. Another result is that the

interaction of He* atoms with the iron oxide surface during MIES takes place via the Auger Neutralization (AN) process. This result is surprising due to the fact that metal oxides usually show an Auger deexcitation (AD) process in MIES. In this case this is not observed due to the high work function of the iron oxide surface and the fact that intrinsic defects result in a Fermi level pinning to the conduction band.

Some publications already investigated the interaction of water with iron films by means of MIES [9–12]. We found that [11] discusses the interaction of H_2O with the system Na/Fe(001). All these references focus on the spin polarization or magnetic properties of the surface. Our focus on the passivating behavior and the formation of an oxide/hydroxide layer on the iron film is not investigated yet.

Thus, another aspect of this publication besides the aspect of corrosion is the investigation of iron surfaces exposed to high water partial pressures by means of MIES. In more detail the interaction path of the He* in front of the H_2O saturated iron surface will be revealed.

The overall scope of this paper is therefore the analysis of the surface reactions between iron films and water molecules under controlled vacuum conditions. XPS, Ultraviolet Photoelectron Spectroscopy (UPS) and MIES are applied to investigate the processes taking place at the topmost surface layer.

2. Experimental

An ultra high vacuum apparatus with a base pressure of $5 \cdot 10^{-11}$ mbar is used to carry out the experiments. All measurements were performed at room temperature.

Electron spectroscopy is performed using a hemispherical analyzer (VSW HA100) in combination with a source for metastable helium atoms (mainly He* $^3S_1$) and ultraviolet photons (He I line). A non-monochromatic X-ray source (Specs RQ20/38C) is utilized for XPS.

X-ray photons hit the surface under an angle of 80° to the surface normal, illuminating a spot of several mm in diameter. The Al K_α line with a photon energy of 1486.6 eV is used for all measurements presented here. Electrons are detected by the hemispherical analyzer with an energy resolution of 1.1 eV under an angle of 10° to the surface normal. All XPS spectra are displayed as a function of binding energy with respect to the Fermi level.

For quantitative XPS analysis, the photoelectron peak areas are calculated after background correction. Especially the strong increase of the inelastic background at the Fe 2p signal has to be corrected with either the method of Tougaard [13] or Shirley [14]. We use the Shirley method as we achieve the most consistent results for our measurements. This was also applied successfully for the interaction of iron with oxygen molecules [8]. Peak fitting with Gauss-type profiles was performed using OriginPro 7 G including the PFM fitting module which uses the Levenberg–Marquardt algorithms to achieve the best agreement possible between experimental data and fit. The quality of the fit is expressed by χ^2 which is returned by the PFM fitting module.

$$\chi^2(P) = \frac{S(P)}{d} = \frac{S(P)}{n^{eff} - p} \tag{1}$$

$S(P)$ denotes the sum of squares of the difference between the data and the fit with P being the parameter vector. The parameter vector P consists of FWHM, peak center and peak area for every used peak. The Levenberg-Marquardt algorithm minimizes $S(P)$ finding the best parameter vector P. Furthermore, d denotes the degree of freedom, n^{eff} is the number of data points used in the fit and p is the number of varying parameters in fitting. For best fit results, we always run the fitting procedure until the fit converges and returns a minimal χ^2 value. To optimize our fitting procedure, Voigt-profiles have been applied to various oxidic and metallic systems but for most systems the Lorentzian contribution converges to 0. Therefore all XPS peaks are fitted with Gaussian shapes. Nevertheless, all results are checked whether they are reasonable and consistent compared to the results by MIES and UPS. We also regard the discussion in literature dealing with this particular topic for iron and its oxides [15,16]. Therefore, we will not deal with any quantitative XPS analysis in this paper.

Photoelectric cross sections as calculated by Scofield [17] and inelastic mean free paths from the NIST database [18] as well as the transmission function of our hemispherical analyzer are taken into account when calculating stoichiometry. Essentially, the peak fitting procedure is done as described in [8].

MIES and UPS are performed applying a cold cathode gas discharge via a two-stage pumping system. A time-of-flight technique is employed to separate He* atoms (for MIES) from HeI photons (for UPS). Electrons emitted by He* interaction with the surface and photoelectrons are detected alternately at a frequency of 2000 Hz. Thus, both spectra are recorded quasi-simultaneously. The recording of such a MIES/UPS spectrum requires 280 s. The combined He*/He I beam strikes the sample surface under an angle of 45° to the surface normal and illuminates a spot of approximately 2 mm in diameter. The spectra are recorded by the hemispherical analyzer with an energy resolution of 220 meV under normal emission.

MIES is an extremely surface sensitive technique probing solely the outermost layer of the sample, because the He* atoms interact with the surface typically 0.3 to 0.5 nm in front of it. This may occur via a number of different mechanisms depending on surface electronic structure and work function, as described in detail elsewhere [19–21]. Only the processes relevant for the spectra presented here shall be discussed shortly:

During AD, an electron from the sample fills the 1s orbital of the impinging He*. Simultaneously, the He 2s electron carrying the excess energy is emitted. The resulting spectra reflect the Surface Density of States (SDOS) directly. AD-MIES and UPS can be compared and allow a distinction between surface and bulk effects. AD takes place for oxide surfaces and metal or semiconductor surfaces with work functions below about 3.5 eV.

The AN process occurs at pure and partly oxidized metal or semiconductor surfaces with work functions beyond 3.5 eV [22,23]. The impinging He* atom is ionized by a resonant transfer (RT) of its 2s electron into unoccupied surface states beyond the Fermi level. Afterwards, the remaining He$^+$ ion is neutralized by a surface electron thus emitting a second surface electron carrying the excess energy. The observed electron spectrum is rather structureless and represents a self convolution of the SDOS.

All MIES and UPS data have been corrected for the analyzer transmission function, that is proportional to E^{-1} in this energy range, where E denotes the kinetic energy of the electrons. The spectra are displayed as a function of the electron binding energy with respect to the Fermi level. The surface work function can be determined from the high binding energy onset of the MIES or the UPS spectra with an accuracy of ± 0.1 eV.

Iron films were prepared by evaporating iron (Goodfellow, 99.95% pure) with a commercial UHV evaporator (Omicron EFM3) onto a tungsten foil with 0.2 mm thickness (PLANSEE Composite Materials GmbH, 99.97% pure). It has been shown previously [8] that W is well suited as substrate, its interaction with iron atoms is negligible. These W foils are polycrystalline. For the growth of iron on W(110) [24] no crystalline growth is expected because of the large misfit of 9.4%. The W target is cleaned from surface contaminations by heating to approximately 1425 K prior to deposition. Iron is subsequently offered at a rate of 0.35 nm/min for 45 min at room temperature. This procedure results in an iron film between 6.4 nm to 9.9 nm thickness as estimated from preliminary XPS measurements. XPS data of freshly prepared iron films are generally showing only small oxygen contaminations well below 10 at.%. Sputtering of a freshly prepared iron film further reduces this contamination. Neither in MIES/UPS nor in XPS can any signal due to the W substrate be detected for an iron film of this thickness.