

Short Communication

Studies of the oxidation of iron by air after being exposed to water vapour using angle-resolved x-ray photoelectron spectroscopy and QUASES™

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Air oxidation of Fe was compared with and without a pre-exposure to water vapour. Angle-resolved x-ray photoelectron spectroscopy (ARXPS) and QUASES™ were used to determine the thickness of the oxide layer formed and its composition. The extent of oxidation was found to be much less if the surface was pre-exposed to water rather than air alone. Studies performed using ARXPS were able to show that the hydroxyl-containing layer located at the surface after Fe was exposed to water vapour was located below the surface after exposure to air. This observation suggested that the oxidation of Fe in air is mediated by cation diffusion. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: ARXPS; QUASES™; Fe; oxidation; passivation

INTRODUCTION

Advances in the analysis of x-ray photoelectron spectra using spectral modelling programs (QUASES™) have led to the completion of in-depth studies of the oxidation of Fe by oxygen¹ and water vapour.² These studies have indicated that oxide films produced by reaction of Fe with water vapour grow with a much lower initial reaction rate than films formed after equivalent exposure to oxygen.² The oxide film formed upon exposure to water vapour (dose = 10⁸ L) at ambient temperature has a FeOOH/Fe₃O₄ duplex structure with a thickness of <2.0 nm², whereas the film formed upon reaction with an equivalent dose of O₂ contains γ -Fe₂O₃ over a layer of Fe₃O₄ and has a thickness of nearly 3.5 nm.¹ The difference in film thickness formed has been suggested to be due to the presence of hydrogen either within^{2,3} or on top of the surface,^{2,4} restricting cationic diffusion as well as the number of sites available for subsequent adsorption during the reaction with water vapour. In addition, the complex conversion of hydroxide to oxide may slow the growth of the oxide layer during the reaction of Fe with water vapour.²

We have studied the effect of the presence of an oxide layer formed in water vapour on the subsequent oxidation of Fe by air using pressures far greater than have been used in the past for similar experiments.^{3,5} Our studies have shown that the thickness of the oxide layer formed

after the surface has been pre-exposed to water vapour is significantly less than if the surface was exposed to air alone. The hydroxide position within the oxide layers formed has been examined using angle-resolved x-ray photoelectron spectroscopy (ARXPS).

EXPERIMENTAL

A pure (99.995%) polycrystalline Fe disc 1.2 cm in diameter (sample 1) was polished to a mirror finish using 0.05 μm γ -Al₂O₃. After being degreased in methanol using an ultrasonic cleaner, it was placed into a Kratos Axis Ultra spectrometer. While under vacuum, the sample was cleaned again using a 4 kV Ar⁺ ion beam for 10 min, followed by a 30 min anneal cycle at 600 °C. After *in vacuo* cleaning, the surface was analysed by XPS to confirm that all contaminant species (C, Na, etc.) had been removed and no oxides remained.

The Fe disc was placed in a second vacuum chamber and exposed to water vapour at a pressure of ~400 Pa for 5 min (dose ~9 × 10⁸ L, T = 24 °C). After dosing, a survey spectrum of the surface was taken using the following parameters: monochromatic Al K α x-ray source, binding energy (BE) range = 1100–0 eV, step size = 0.7 eV, pass energy = 160 eV, sweep time = 180 s and number of sweeps = 8. High-resolution spectra (Fe 2p, O 1s and C 1s) were also collected using a 20–40 eV window, depending on the peak analysed, and a pass energy of 40 eV. After analysis was complete, the surface was oxidized in air at atmospheric pressure (relative humidity = 32–37%, T = 20–22 °C) for

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2 min (dose $\sim 9 \times 10^{10}$ L) before being placed back in the vacuum and re-analysed. After this analysis was complete, the surface was cleaned and annealed again in a vacuum and then exposed to air at atmospheric pressure for 1 min (dose $\sim 5 \times 10^{10}$ L) without receiving a water vapour pre-treatment and analysed using the parameters provided above.

For ARXPS experiments, a second sample (sample 2) was prepared and cleaned in the same manner discussed above and then exposed to water vapour at ambient temperature for 5 min at a pressure of ~ 400 Pa (dose $\sim 9 \times 10^8$ L). After exposure, the surface was analysed by ARXPS using electron take-off angles of 90° , 48° , 30° and 15° . Both survey and high-resolution (Fe 2p, O 1s and C 1s) spectra were collected. After the analysis was complete, the surface was exposed to air (relative humidity = 32–35%) at atmospheric pressure and ambient temperature for 2 min (dose $\sim 9 \times 10^{10}$ L) and re-analysed by ARXPS.

All spectra were analysed using the CasaXPS software.⁶ Peak shifts due to any charging were normalized with the C 1s peak from adventitious carbon set to 284.8 eV. The Fe 2p high-resolution spectra were fitted using Gupta–Sen multiplet peaks^{1,2,7–10} to determine the presence of Fe^{2+} and Fe^{3+} oxide/hydroxide species. High-resolution O 1s spectra also were analysed to determine the presence of oxide/hydroxide species.

The Fe 2p and O 1s peaks found in the survey spectra taken were analysed by QUASES™ Analyze and Generate to determine the thickness and composition of some of the oxide layers formed. ‘Analyze’ models the extrinsic background of a photoelectron peak due in most part to

inelastic electron scattering causing energy loss, allowing one to determine the depth range over which particular elements are distributed.^{11,12} ‘Generate’, on the other hand, allows the experimental spectrum to be modelled using various combinations of reference spectra (to a maximum of three) whose extrinsic backgrounds have been altered based on the depth at which they are found within the surface.^{11,12} More information on how these programs can be used to determine the thickness of the oxide layers is provided in Refs 1, 2, and 12. A detailed discussion of the theory behind QUASES™ can be found in Ref. 13. It should be noted that the success of the QUASES™ analysis is dependent on the cross-section of inelastic electron scattering and the attenuation lengths used. During this research, the universal cross-section developed by Tougaard¹⁴ was used, as well as the following attenuation lengths (AL, λ): $\lambda_{\text{Fe}} = 1.3$ nm, $\lambda_{\text{Fe}_3\text{O}_4} = 1.4$ nm, $\lambda_{\text{Fe}_2\text{O}_3} = 1.4$ nm and $\lambda_{\text{FeOOH}} = 1.4$ nm.²

RESULTS AND DISCUSSION

Figure 1 shows the high-resolution Fe 2p_{3/2} and O 1s XP spectra from the surface of sample 1 after being exposed to water vapour (Figs 1(a) and 1(d)), followed by an air oxidation treatment (Figs 1(b) and 1(e)). The spectra from the same surface oxidized only in air are also shown (Figs 1(c) and 1(f)). The Fe 2p_{3/2} and O 1s spectra collected after the sample was oxidized with water vapour (Figs 1(a) and 1(d)) are virtually identical to those found during an earlier oxidation study involving water vapour.² The surface was found to contain Fe oxides as well as hydroxides or

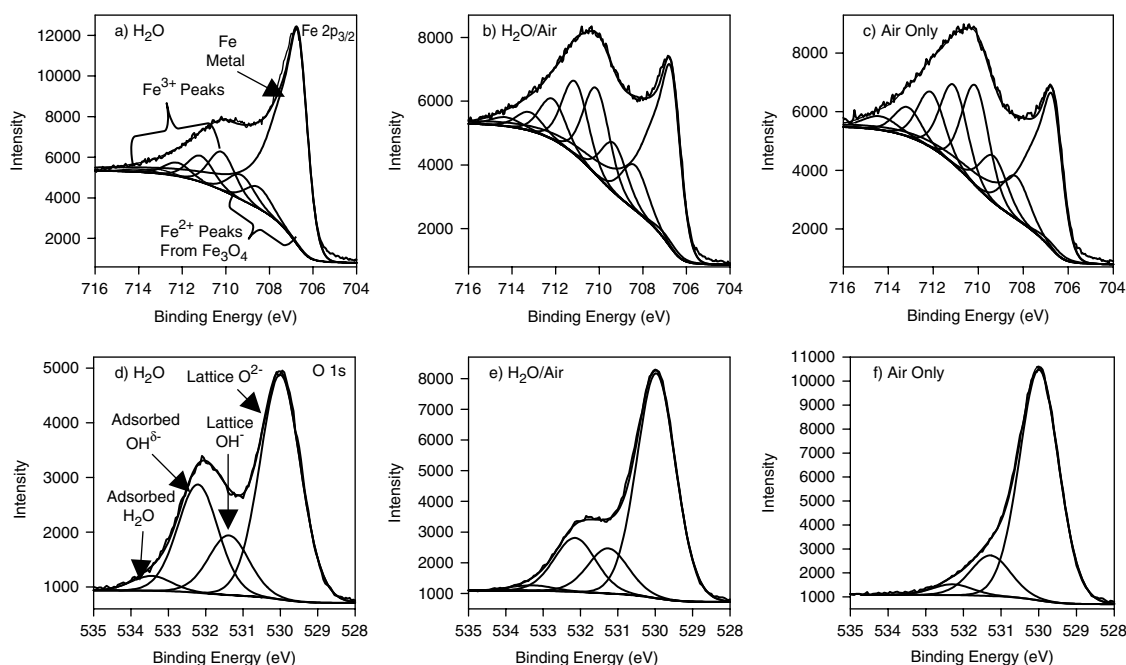


Figure 1. The Fe 2p_{3/2} and O 1s high-resolution XPS spectra from the surface of sample 1 after exposure to water vapour (a, d), water vapour and then air (b, e) and air only (c, f). The Fe 2p_{3/2} Gupta–Sen multiplet peaks pertaining to Fe^{2+} and Fe^{3+} have been labelled in Fig. 1(a), as well as the asymmetric peak pertaining to Fe metal. The Fe^{3+} components in Figs 1(a)–1(c) correspond to Fe_3O_4 and FeOOH . Peaks from Fe^{3+} corresponding to $\gamma\text{-Fe}_2\text{O}_3$ are also expected to be present in Figs 1(b) and 1(c). The individual oxide species found in the O 1s spectra are indicated in Fig. 1(d). All spectra were fitted using a Shirley-type background. Figure 1(f) was not found to contain a peak pertaining to adsorbed water vapour. All spectra were collected using an electron take-off angle of 90° .

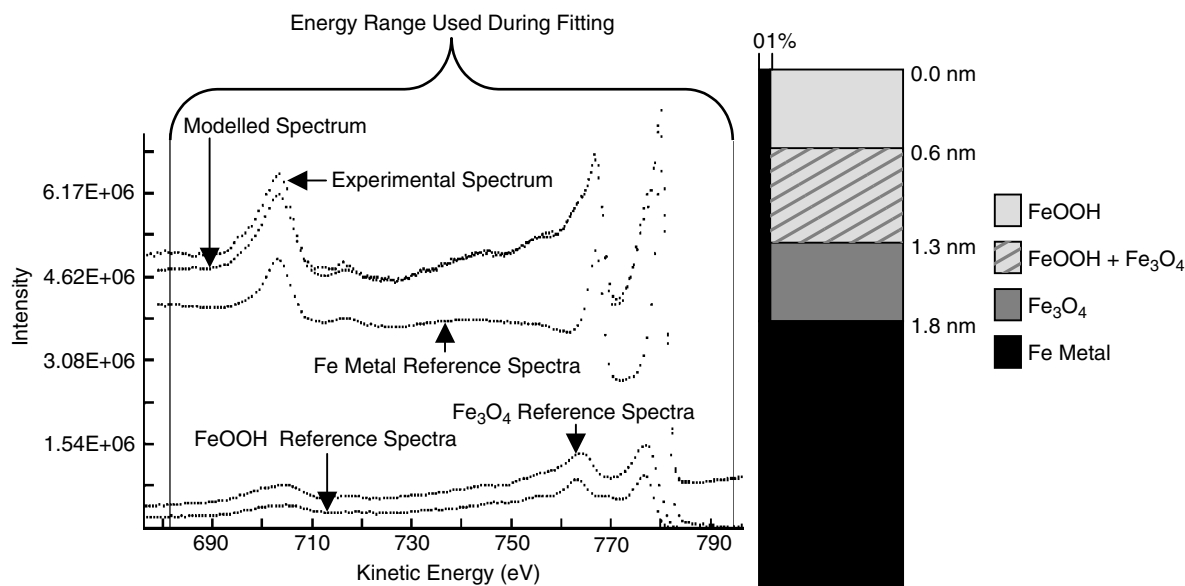


Figure 2. The QUASES™ Generate results, indicating the composition and thickness of the oxide layer formed upon exposure of clean Fe metal (sample 1) to water vapour at ambient temperature until a dose of 9×10^8 L was reached. The spectral results also have been included in this figure. The model spectrum was found to overlap completely with the experimental results in the range 720–780 eV.

oxyhydroxides, regardless of the reaction conditions used. For the water vapour exposure, QUASES™ Generate analysis of the Fe 2p spectrum (Fig. 2) was able to determine that the oxide structure consisted of FeOOH on top of a layer of Fe₃O₄ with a total thickness of 1.8 nm. The presence of some Fe metal within the oxide layer is attributed to unreacted metal grain interiors.

Turning to the O 1s spectra in Fig. 1, the spectrum from the surface exposed to water vapour followed by air (Fig. 1(e)) indicated a significant quantity of lattice OH⁻ (531.3 ± 0.1 eV)² as well as considerable quantities of adsorbed OH^{δ-} (532.1 ± 0.1 eV)² and adsorbed H₂O (533.3 ± 0.3 eV).² By contrast, the O 1s spectrum from the air-oxidized surface that was not pretreated with water vapour (Fig. 1(f)) contained lower concentrations of lattice OH⁻ and adsorbed OH^{δ-} species. The presence of these peaks is attributed to the relative humidity of the air that the surface was exposed to. In both spectra, lattice O²⁻ was the predominant species.

Unfortunately, QUASES™ Generate was unable to produce a satisfactory analysis of the Fe 2p spectra from the two surfaces after exposure to air because the layer structures were too complex: they contained more than three species within the surface volume analysed. However, QUASES™ Analyze was able to produce a consistent analysis of the total oxide thickness for each surface. These results indicated that the thickness of oxide formed on the water-pretreated Fe surface was significantly less than the thickness of oxide formed on the surface that received no water pretreatment (2.3 nm vs. 3.2 nm). This observation was found despite the fact that the surface exposed to air alone received a dose only half as large as the dose given to the surface that was pre-exposed to water vapour. The large difference in oxide thickness indicates a decrease in the reaction kinetics for the reaction of air with the water-pretreated surface compared with the surface that was not pre-exposed to water.

The remarkable effect of a 1.8 nm thick layer of FeOOH/Fe₃O₄ on the subsequent oxide growth rate of Fe with air lends to our perception that any involvement of water vapour will compromise the oxide growth. Other researchers^{3,5} have also noted the apparent passivating effects of water, although not under the ambient conditions examined in this work. A relevant question concerning the initial FeOOH/Fe₃O₄ layer is whether the hydroxide functionality remains intact within the oxide layer after exposure to air?

In the absence of a satisfactory QUASES™ Generate analysis of the inner structure, ARXPS was used to compare the depth distributions of the lattice hydroxide (OH⁻) and lattice oxide (O²⁻) populations for an Fe surface (sample 2) exposed to water vapour only and water vapour followed by air. Figure 3 compares the relative change in the concentration of lattice O²⁻ and lattice OH⁻ species with electron take-off angle after exposure to water vapour only and water vapour followed by exposure to air. The QUASES™ Generate analysis (not shown) of the surface exposed to water vapour alone showed that the lattice OH⁻ component was distributed preferentially at the outermost surface (0.8 nm thick FeOOH layer over top of Fe₃O₄). As such, this provides a benchmark against which the distribution of lattice OH⁻ in the water-pretreated air-oxidized surface can be compared. It would appear that the OH⁻ containing layer either lies below the surface after exposure to air or its reach has extended further into the oxide layer, allowing the results shown in Fig. 3 to have a decreased slope compared with those found after the surface was exposed to water vapour alone.

The ARXPS results were analysed using an algorithm (ARXPS Version 3)¹⁵ developed by Paynter¹⁶ that can extract depth information using a boxcar model. This analysis allowed the change in concentration of the O²⁻ and OH⁻ components with changing electron take-off angle

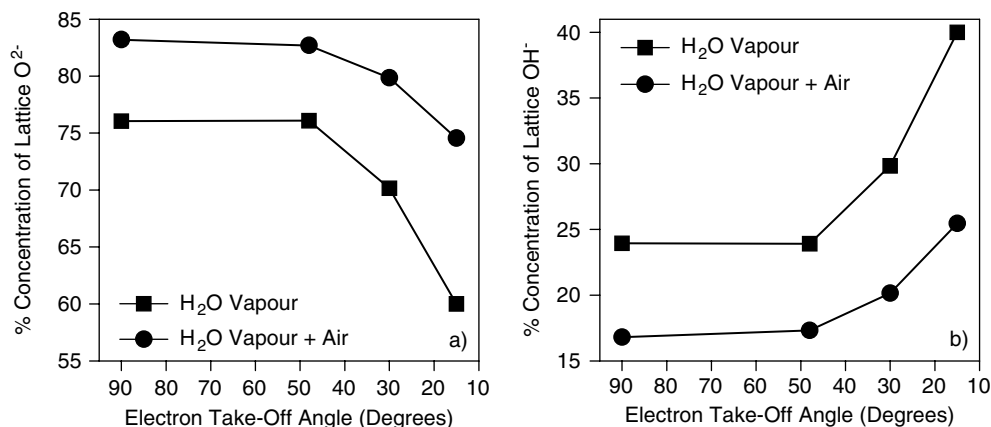


Figure 3. Plots of the change in the lattice O²⁻ concentration (a) and lattice OH⁻ concentration (b) with decreasing electron take-off angle for the surface of sample 2 exposed to water vapour and to water vapour followed by exposure to air. Results were taken from analysis of the high-resolution O 1s XPS spectra taken at different electron take-off angles. The results found at the highest angle (90°) represent contributions stemming from 100% of the maximum electron escape depth, whereas the results found at the lowest angle (15°) represent contributions stemming from only 26% of the electron escape depth.

to be modelled, and from this a depth distribution was approximated. The calculated depth distributions for the water vapour-exposed and water vapour plus air-exposed surfaces, shown in Fig. 4 (solid lines), indicated that the lattice OH⁻ component extended deeper for the water vapour and air-exposed surface than for the surface exposed to water vapour alone. The thickness of the OH⁻-containing layer for the surface exposed to water vapour alone matches well with the thickness of the surface layer of FeOOH determined using QUASES™ Generate (0.8 nm). The OH⁻/O²⁻ ratio found in this layer was 0.7:1, which confirmed the presence of FeOOH.

The boxcar model used during analysis of the ARXPS results assumes a solid overlayer on a substrate. This assumption therefore does not allow a resolvable subsurface OH⁻ layer to be modelled. The layer formed after exposure

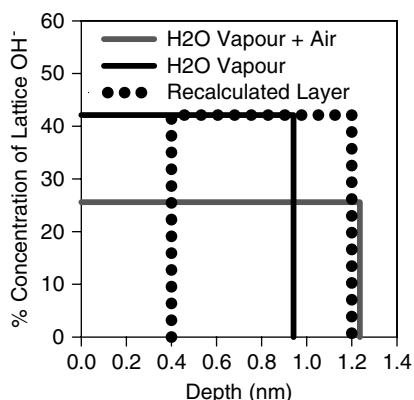


Figure 4. Boxcar model depth profiles of the lattice OH⁻ concentration determined from the ARXPS data for the surface of sample 2 exposed to water vapour and to water vapour followed by air (solid lines). The analysis was performed using ARXPS Version 3¹⁵ and the algorithm developed by Paynter.¹⁶ The recalculated layer showing the predicted subsurface hydroxide-containing layer after exposure of Fe to water vapour and then air is indicated by the dotted line.

to water vapour and then air (shown in Fig. 4) indicates that the concentration of oxygen within the film contains ~26% OH⁻; this is far less than is found in a layer containing FeOOH only (50%). It should be noted, however, that the area in the oxide layers found to contain lattice OH⁻ (shown in Fig. 4) are approximately the same regardless of the oxidation treatment used. This indicates that the thickness of the OH⁻-containing layers in the two oxide films should be essentially the same if one assumes an equal concentration of OH⁻. Using the OH⁻ concentration found for the surface after exposure to water vapour only (~42% of the total oxygen concentration), the FeOOH layer in the oxide formed after exposure of Fe to water vapour and then air beginning 1.2 nm below the surface was recalculated to be 0.8 nm thick, with a 0.4 nm overlayer presumably containing Fe oxide(s) that would form via cation diffusion. This new recalculated layer is also shown in Fig. 4 (dotted line). The thickness of this FeOOH layer is the same as the value predicted by QUASES™ Generate for the layer formed when only water vapour was used as the oxidant.

CONCLUSIONS

The pre-oxidation of Fe by water vapour has been investigated and found to increase the passivation of the surface towards further oxidation by air. Angle-resolved XPS of an Fe surface exposed to water and then air indicated that the oxyhydroxide layer located at the surface of the Fe, which was formed upon reaction with water vapour, was located below the surface after further oxidation with air. These results suggest that oxidation of Fe by air under these conditions is mediated by cation diffusion.

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