



Corrosion of aluminium components studied with MIES, UPS and XPS

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Abstract

We use X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and metastable impact electron spectroscopy (MIES) to investigate the corrosion of aluminium components. Clean aluminium films were prepared under ultrahigh vacuum (UHV) conditions and exposed to water and NaCl. We attempt to provide a model for the mechanism of this interaction and its effects on the durability of the components.

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1. Introduction

Corrosion, especially atmospheric corrosion, has been a subject of engineering studies, largely empirical, for nearly a century [1]. The interaction of oxygen with single and polycrystalline aluminium surfaces has been extensively studied in the past [2,3], but corrosion is mostly induced by a watery environment. Because metastable impact electron spectroscopy (MIES) is one of the most surface-sensitive techniques, we applied it to the H₂O

interaction with Al-films. Previous examinations were done by soft X-ray photoemission spectroscopy (XPS) [2], therefore bulk and surface effects during the water adsorption have not been compared yet.

2. Experimental

The apparatus was described in detail previously [4]. Briefly, it is equipped with a hemispherical analyzer (VSW HA 100) in combination with He⁺/HeI and an X-ray source. MIES and ultraviolet photoelectron spectroscopy (UPS) are performed applying a cold-cathode discharge adapted to the ultrahigh

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vacuum chamber via a two-stage pumping system. A time-of-flight technique is integrated to separate electrons emitted by He* (MIES) and HeI (UPS) interaction with the surface. MIES and UPS spectra are recorded with a resolution of 250 meV under normal emission within 100 s. Longer integration times are not possible without rising of gas exposure inaccuracies. The angle of incidence for the mixed He*/HeI beam is 45°. XPS is performed using a commercial X-ray source (Specs RQ20/38C). The photons hit the surface at an angle of 80° to the surface normal. Emitted electrons are analyzed at 10° to the surface normal with a resolution of 1.2 eV. The base pressure of the apparatus is 2×10^{-11} mbar.

Metastable He* atoms may interact via different mechanisms depending on surface electronic structure and work function. For the surfaces studied here only Auger deexcitation (AD) and Auger neutralization (AN) occur. During AD an electron from the sample surface fills the 1s orbital of the impinging He*. Simultaneously, the He* 2s electron is emitted carrying the excess energy. In contrast, AN is a 2-step process. Approaching the surface, the He* 2s electron is resonantly transferred into unoccupied states of the sample surface. Subsequently, an electron from the surface fills He+ 1s, thus emitting another electron from the surface. The resulting spectra display a self-convolution of the surface density of states (SDOS). Detailed descriptions of these processes may be found in recent reviews [5,6].

Al films were produced by evaporating Al from a commercial metal evaporator (Omicron EFM3) at a flux of about 0.65 ML min^{-1} . These layers were produced on clean Si(100) [7] targets at room temperature. The quality of these films was checked by MIES and XPS. Typical film thicknesses amount to 10 ML, estimated by the attenuation of the Si 2s/Si 2p peaks after Al offer in XPS.

H₂O is offered by backfilling the chamber. Several pump-freeze cycles were done for cleaning the water. NaCl is evaporated by a home built evaporator [8].

All MIES and UPS spectra are displayed as a function of the electron binding energy with respect to the Fermi level, which is determined by the high-energy cut-off obtained on metallic samples in UPS and MIES. The surface work function can be determined from the low-energy onset of the MIES or the UPS spectra with an accuracy of ± 0.1 eV.

3. Results and discussion

Fig. 1a shows the MIES-spectra obtained during H₂O-exposure of an Al film, and Fig. 1b shows the corresponding UPS-spectra. The bottom spectra present the result for the clean Al film. MIES is dominated by AN. The UPS spectrum of the clean Al film shows the metallic contribution (Al 3p) directly at the Fermi edge ($E_B = 0$ eV). During the water exposure the change from AN to the AD process is seen in MIES. After an exposure to about 10 L H₂O both MIES and UPS show the development of a peak at 7.7 eV (MIES) and 7.4 eV (UPS), respectively. For exposures to about 150 L, MIES shows a second peak at 12.3 eV, in UPS a second peak is observed at 13.5 eV. In both MIES and UPS the peak around 7.5 eV is donated by the O(2p)-orbital, as the comparison with experiments on the O₂-Al interaction [2,3] shows. Molecular adsorption of H₂O can be excluded, because this would lead to the well-known three-peak structure in MIES and UPS [9,10]. The peak at 12.3 eV in MIES originates from OH⁻ groups on top of the surface. In contrast, UPS shows a small additional peak at 13.5 eV, which is not seen in MIES. To clear up these observations, further experiments (not shown here) were performed in a high-pressure cell, which is directly adapted to the vacuum chamber [11]. An Al film produced as described above was exposed to 8 mbar H₂O for 70 h. Under these conditions the Al film is completely transformed to Al(OH)₃ [12]. MIES and UPS measurements of this surface suggest that the observed structures (see Fig. 1) are donated by Al(OH)₃ contributions.

Fig. 2 shows the water adsorption after the co-deposition of half a monolayer of NaCl and about 90 L H₂O. The bottom spectra were taken after this co-deposition. Therefore, neither MIES nor UPS show a spectrum similar to the clean Al film. Both techniques show a peak at about 7.8 eV. We assume this peak to be donated mostly by O(2p)-orbitals, partly by Cl⁻(3p) on top of the surface. XPS spectra (not shown here) observed after the co-deposition show strong O(1s) contributions and only weak Cl(2p) ones. In UPS, the metallic contribution at the Fermi edge is still visible. During the water adsorption the behaviour is similar to the H₂O exposure of the clean film: in MIES a peak at 12.4 eV is growing, and in

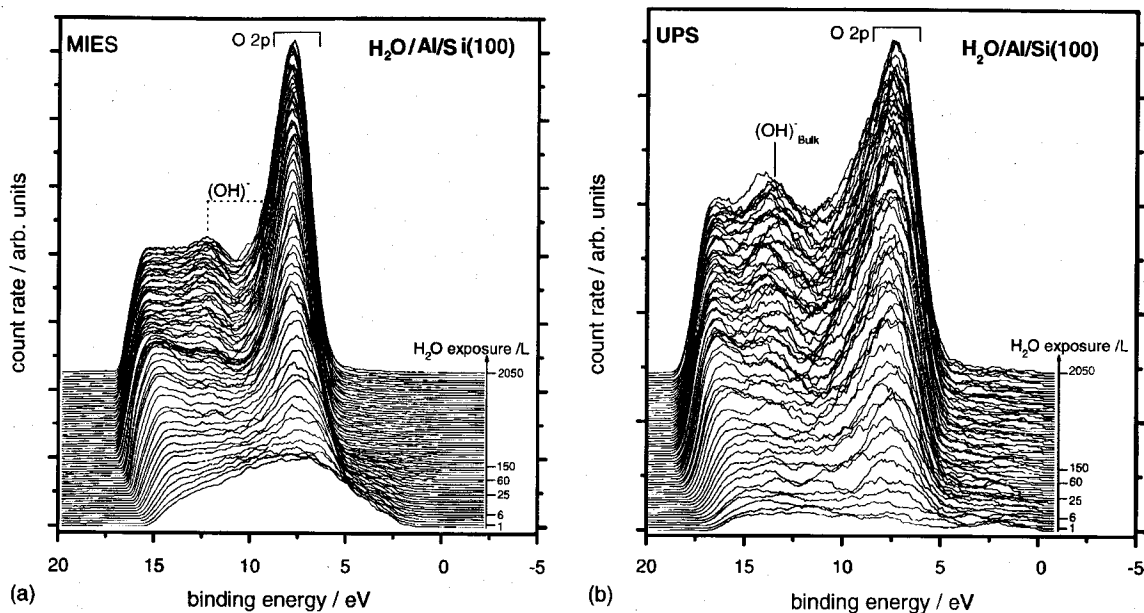
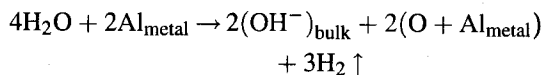


Fig. 1. (a) MIES spectra of an Al film during its exposure to H₂O at room temperature. The bottom spectrum shows the clean Al film, the top spectrum shows the Al film after the exposure to 2050 L of H₂O. (b) UPS spectra that are simultaneously recorded with the MIES spectra in (a).

UPS a peak at 13.4 eV. In UPS this peak is already seen in the first spectra. Therefore, we conclude that aluminium hydroxide is already forming in the subsurface layers during the co-deposition. We found these peaks to be smaller than the ones shown in Fig. 1. The comparison of both experiments shows the following effects: the development of the work function gives evidence that the oxidation of the aluminium surface is much faster with NaCl co-deposition. XPS measurements of the Al(2p)-structure (Fig. 3) show that the thickness of the resulting oxide layer after the NaCl + H₂O co-deposition (2.83 nm, estimated on the calculations of McCafferty and Wightman [13]) is slightly thicker than after the pure H₂O exposure (2.45 nm). Our XPS measurements before and after the water exposure on the NaCl-covered Al film (not shown here) show a decrease of the Cl(2p) intensity.

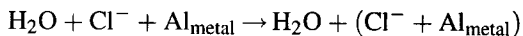
Therefore, we propose the following reaction model: impinging water molecules dissociate in front of the aluminium surface. Oxygen atoms are incorporated in the subsurface region, thus forming an amorphous oxide layer [14], as it is indicated by a decrease of the work function. UPS shows that OH⁻

is partially incorporated in the sub-surface layers of the aluminium bulk, forming an aluminium hydroxide:

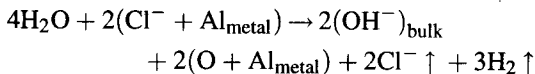


This assumption is supported by the work of Olefjord and Nylund [12], basing on their high-resolution XPS experiments.

The adsorption of H₂O after the NaCl + H₂O co-deposition proceeds in a different way: in the first step during the co-deposition the Cl⁻ ions from the NaCl are adsorbed on the surface:



In a second step an exchange of the Cl⁻ and oxygen atoms from the impinging H₂O molecules takes place [1]:



As the H₂O adsorption results in a much faster saturation after the H₂O + NaCl co-deposition, we assume that the presence of the Cl⁻ enhances the possibility

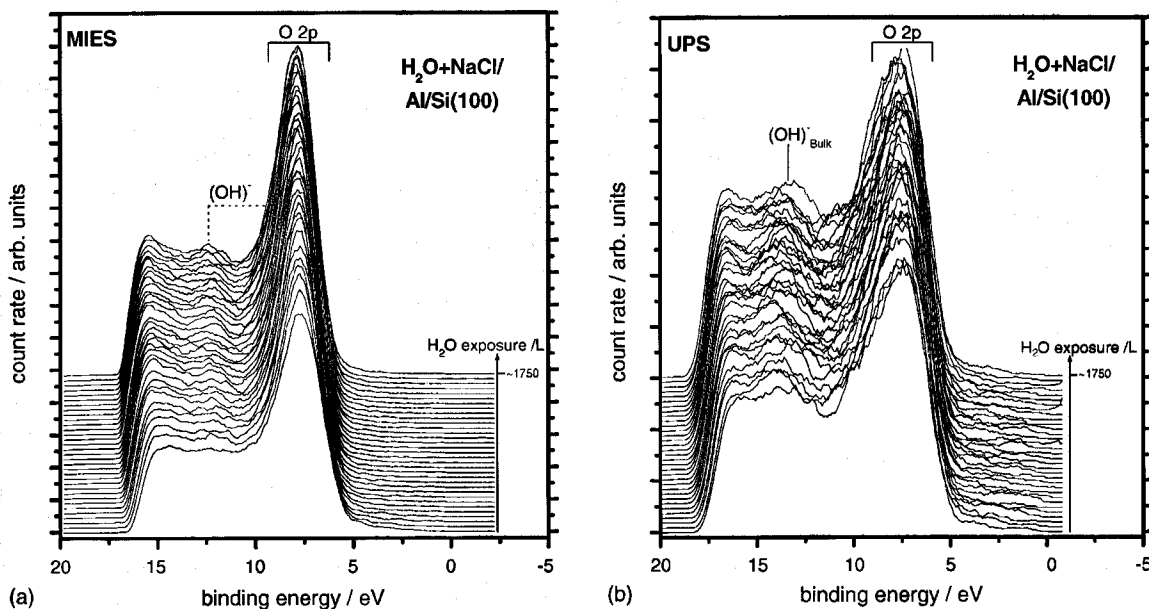


Fig. 2. (a) MIES spectra of the H₂O exposure after the co-deposition of half a monolayer of NaCl and 90 L H₂O on top of an Al film. The bottom spectrum shows the NaCl + H₂O covered Al film, the top spectra shows it after exposure to 1750 L H₂O. (b) UPS spectra that are simultaneously recorded with the MIES spectra in (a).

for the dissociation of the impinging H₂O molecules. This enhanced dissociation probability may cause the observation that the OH contributions after NaCl deposition are lower.

4. Summary

We report electron spectroscopy (MIES and UPS) results for the interaction of H₂O with

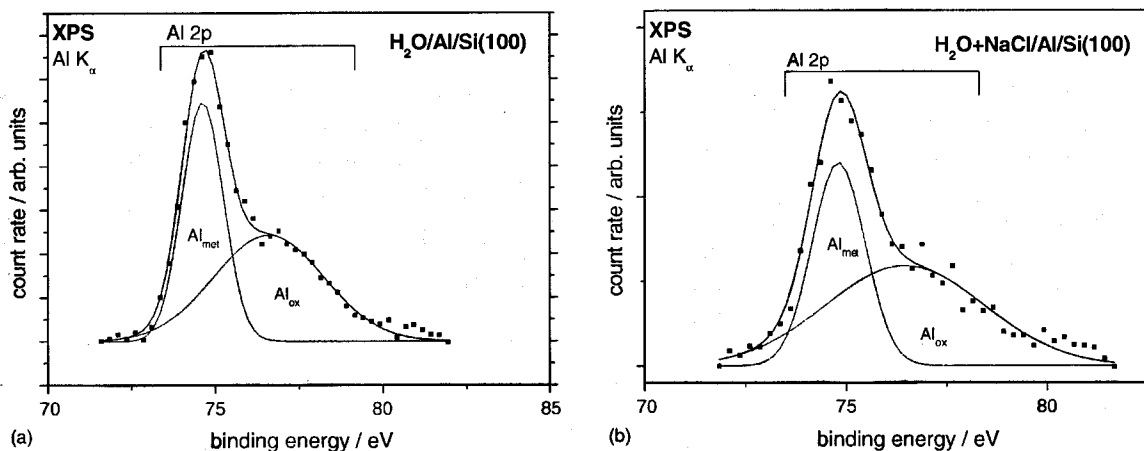


Fig. 3. (a) XPS spectrum of the Al(2p) peak after the H₂O exposure (corresponding to the top spectra in Fig. 1). The rectangles represent the experimental data. The line shows a Gaussian fit. (b) XPS spectrum of the Al(2p) peak after the co-deposition experiment (corresponding to the top spectra in Fig. 2).

aluminium films at room temperature. The water dissociates, leading to the formation of an amorphous oxide film. Additionally, a small amount of hydroxide formation in the subsurface region is observed. On top of the surface OH^- is only adsorbed at defects. For comparison, we report the results of the interaction of water with aluminium after the co-deposition of half a monolayer of NaCl and 90 L H_2O . The presence of Cl^- on the surface enhances the dissociation of the water. This accelerates the formation of the amorphous oxide and results in a thicker oxide film. The Cl^- desorb from the surface during this process.

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