

In-situ-FTIR-spectroscopic studies of organic acid monolayers on metal oxides in humid environments

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Abstract

A new in-situ setup combining ultra-high vacuum (UHV), plasma application, modern photoelastic-modulated-infrared-reflection-absorption-spectroscopy (PM-IRRAS) and quartz crystal microbalance (QCM) was developed to analyze the formation and stability of self-assembled monolayers (SAMs) on engineering metals in detail.

At first the adsorption behaviour of different organophosphonic acids on nickel-titanium (NiTi) shape memory alloy (SMA) were analysed. PM-IRRAS prove that the binding mechanism is based on a mono- or bidental bond. In addition it was shown that an alkyl chain length of 17 CH₂ groups is required for the formation of a SAM, which is stable in aqueous environment.

Furthermore in-situ measurements were undertaken to determine the formation, the barrier properties and the stability under high water activities of octadecylphosphonic acid (ODPA) and nonadecanoic acid (NDA) SAMs. PM-IRRAS reveal the self-assembly of both molecules on oxyhydroxide covered aluminium surfaces and prove their stability during exposure to humid air.

For ODPA and NDA SAMs a strongly reduced amount of water – based on the inability of water to form hydrogen bonds to the low energy aliphatic surfaces – was observed.

However, the ODPA monolayer covered surfaces did not show a significant inhibition of the H₂O/D₂O isotope exchange reaction between a D₂O gas phase and the hydroxyl groups of the aluminium oxyhydroxide film. The high stability of the interfacial phosphonate group as well as the constant ordering of the SAM are referred to the strong acid-base interaction of the phosphonate head group with the Al ions as well as the molecular interactions of the aliphatic chains.

For NDA monolayer covered Al substrates the kinetic of surface hydroxylation by dissociative adsorption of H₂O molecules could be significantly reduced while the interfacial carboxylate group as well as the orientation of the NDA monolayer is not affected by the adsorption of water.