FORMATION AND STRUCTURE OF ALKYL PHOSPHONIC ACID LAYERS ON IRON

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Surface modification of metals by organic thin films, such as self-assembling molecules is a new encouraging method of corrosion protection, which might be able to replace environmentally restricted surface treatments. Self-assembled monolayers (SAMs) can exceed the corrosion protection effect of commonly used inhibitors due to the attractive interaction between molecules in the ordered, dense structure. Long-chain molecules, terminated in inhibitive functional groups are the most promising molecules in practical aspects.

The objective of our studies was to elaborate protective films against corrosion by the application of self-assembling molecules of phosphonic acid termination. Systematically changed molecule-series of alkane-mono- and diphosphonic acids were investigated on Armco iron surface in neutral aerated aqueous solutions. The layer formation was monitored indirectly by using linear voltammetry and impedance spectroscopy.

The layer formation proved to be a spontaneous process on iron, and could be accomplished by simple immersion of the substrate into the neutral or alkaline aqueous solutions of phosphono compounds, resulting in a thin dense adsorption layer with a high corrosion protection effect. The influence of the phosphonate treatment on impedance spectra of iron is shown in Fig. 1, the increased impedance of modified iron is related to the high protective effect of closed-packed thin layer. The corrosion protection mechanism of ordered molecular monophosphonic acid films were also investigated. The molecules act as anodic corrosion inhibitors, significantly reducing iron dissolution.

The role of oxide in the surface interaction of phosphono groups has been proved to be important, as systematic pre-passivation of the iron surface resulted in a gradual stabilization of the evolving self-assembled protecting layer (Fig. 2). Ex-situ morphology of modified iron surface has been followed by atomic force microscopy (Fig. 3). As a comparison, structural studies on self-assembly of phosphonic acids were carried out on atomically flat mica surface.

Diphosphonic acids may have a potential role in practical surface pretreatment, as the two functional groups act as a bridge between a metal and organic coating. Such a way the diphosphonic acids can protect metal dissolution and assist to paint adhesion at the same time. "Self-healing" properties of the layers have been demonstrated by scratching the protective layer and observing the restoration of electrochemical properties in short time scale. In practical three-phase system (metal / diphosphonic acid / organic coating) the diphoshonic acid significantly increased the corrosion resistance of the coated metal.
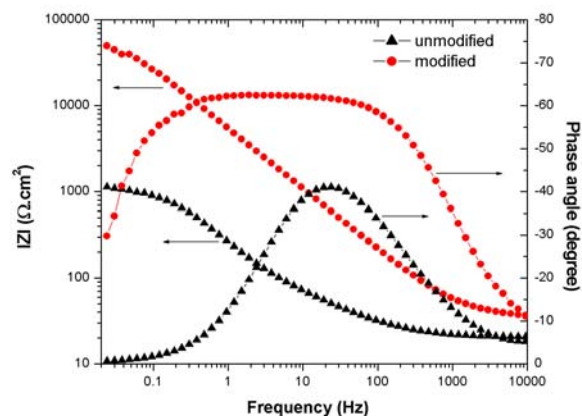

Figure 1. Impedance (Bode) plot of modified and unmodified Armco iron in 0.1 M NaClO$_4$ solution. Surface modification of iron: immersion in 1-phosphono-octane solution (pH=7) for 4 days. (Polarization resistance values: untreated 1.2 kΩ.cm^2; treated: 67.5 kΩ.cm^2)
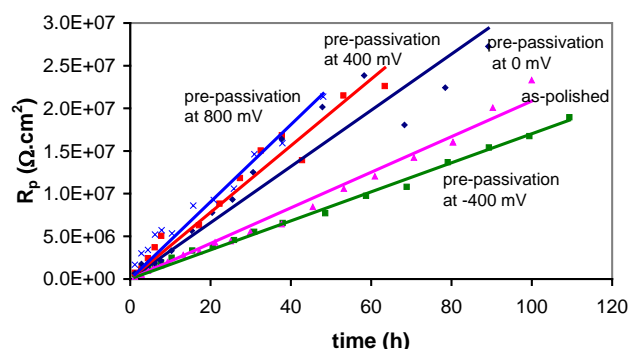

Figure 2. Change of polarization resistance of Armco iron in 10^{-3} M 1-phosphono-octane solution (pH=7) after potentiostatic passivation in borate buffer (pH=8.4) for 60 min at different potentials
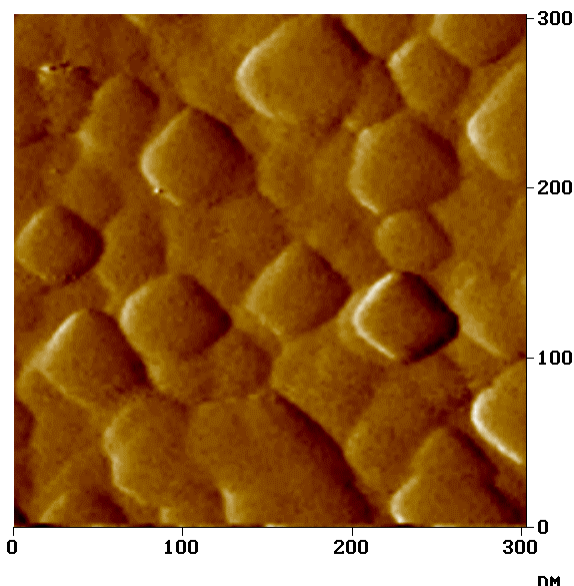

Figure 3. Atomic force microscope image of iron pre-passivated in borate buffer (pH=8.4) for 60 min at 400 mV/SCE and immersed into 10^{-3} M 1-phosphono-octane for 6 days