Abstract

It has been reported that 1/5 of energy globally and an average of 4.2% gross national product (GNP) is lost each year due to corrosion demage. Despite numerous studies and the enormous damage caused by corrosion in various industrial fields (mechanical engineering, civil engineering, shipping, aviation, electroengineering) the solution is still not viable. Every step against corrosion with effective protection is therefore very important. Recently huge effort has been devoted to development of sol-gel anti-corrosion coatings based on organic-inorganic hybrids with nanocomposite structure. The sol-gel process enable introduction of multifunctional properties to material, which can reduce the thickness of protective layers, which still retain low permeability for oxygen and ionizing species. The advantage of sol-gel coatings is the formation of covalent bonds with metals, leading to good adhesion of sol-gel layers.

This thesis connects two aspects of materials chemistry, starting with the development of new materials by the sol-gel process, and continuing with the development of analytical techniques for the study of these materials. We have synthesized and studied the anticorrosion protective layers for the aluminum alloy AA 2024. Three kinds of protective coatings have been prepared and applied on substate with a dip-coating technique. Parallelly with the research of materials we applied advanced analytical tools. An *ex situ* IR RA technique has already been used in our laboratory, while *in situ* Raman spectroelectrochemical cell and *in situ* electrochemical AFM cell have been constructed as a part of this Ph.D. work. Both *in situ* cells enable simultaneous measurements with electrochemical and spectroscopic/AFM technique and allow a deeper insight into the processes that occur in the protective coating during the accelerated degradation processes. Such combined results are valuable and enable iterative improvement of prepared materials.

The first type of protective coatings based on 1,2-bis(trimethoxysilyl)ethane (BTMSE), and was mainly used to study the degradation of the coating surface during the anodic polarization. *In situ* AFM electrochemical results showed a reduction in the surface roughness during the degradation process. These observations were confirmed by *ex situ* IR RA spectroscopic measurements, which showed visible changes in hydration of coatings, breaking of certain siloxane Si-O-Si and Si-O-Al bonds, and changes in the C-H vibration region.

The second part of this doctoral thesis is based on the development and characterization of protective coatings prepared from the cyclic siloxane precursor 1,3,5,7-tetramethyl-1,3,5,7-

tetra(2-(3-trimethoxysilyl)propyl sulfanyl)ethyl ciklotetrasiloxane (CS4) (synthesized in our laboratory). This compound was used alone and in combination with other sol-gel precursors, which were added in order to increase the crosslinking of the coatings. One of the main objectives of our work was to determine whether the cyclic precursor, due to its structure can be more effective for the production of anticorrosion coatings as silanes with a simpler structure. We found that the combination of silanes gave the best results.

The third type of protective coatings based on epoxypropoxypropyl terminated polydimethilsiloxane (EP-PDMS-EP), crosslinked with an organic-inorganic hybrid aminopropylsilane (APTMS). In these coatings we include various concentrations of aminopropyl-heptyl-isooctyl polyhedral oligomeric silsesqoxane (AP-iOc$_7$-POSS) to evaluate its impact on protective properties. We have found that the increasing amount of POSS molecules improve the efficiency of corrosion protection.

For the latter two types of coatings we used *in situ* Raman spectroelectrochemical studies. We observed intensity decrese of all bands and the formation of pitting corrosion.

Keywords: organic-inorganic hybrids, corrosion protection, *ex situ* IR RA, *in situ* AFM, *in situ* Raman