

Abstract

We prepared a coating on the basis of (3glycidoxypropyl)trimethoxysilane (GPTMS) for the aluminium alloy AA 2024-T3. GPTMS was crosslinked with the addition of three different primary amines, (3-aminopropyl)trimethoxysilane (APTMS), aminopropyl terminated polydimethylsiloxane ($\text{H}_2\text{N-PDMS-NH}_2$) and aminopropyl (heptaisooctyl) polyhedral oligomeric silsesquioxane (AP-iOc₇-POSS). Electrochemical measurements have shown a degree of dependence of corrosion protection on the content of polydimethylsiloxane chains (PDMS) in the coating, but too high a content of PDMS chains became detrimental. Those results were confirmed by the free surface energy measurements, which showed a decrease of free surface energy with the increase of PDMS. Hydrolysis and condensation of sols was monitored by infrared (IR) absorption spectroscopy and rheological measurements to determine the most suitable time for the coating deposition, which was 30 min after the addition of the acid catalyst, i.e. acetic acid. The coatings were also tested by *ex situ* spectroelectrochemical measurements with IR reflection-absorption (IR RA) and Raman spectroscopy. The measurements have been carried out before and during the anodic polarization of the samples. The measured IR RA spectra showed the beginning of the cleavage of siloxane bonds and the formation of lower cyclosiloxanes and hydration. In coatings without PDMS chains we detected a shift in the C-H vibration range. *Ex situ* Raman spectroelectrochemical measurements of coatings with PDMS chains after anodic polarisation showed mainly PDMS bands on an optically intact part of the coating, but with a declined intensity. Where pitting corrosion appeared we no longer could detect the presence of any signals. On the basis of valence $\nu(\text{Si-O-Si})$ vibrations of the condensed sol-gel network at 476 cm^{-1} we could not confirm the formation of the band associated with lower cyclosiloxanes because of the presence of siloxane vibrations in the PDMS chains at 496 cm^{-1} .

As an alternative protection we prepared sols on the basis of a bis end-capped silanol, bis-(3-(3-(3-triethoxysilyl)propyl)thioureido)propyl terminated polydimethylsiloxane (PDMSTU), with the addition of bis-(3-(3-(3-triethoxysilyl)propyl)tetrasulphide (BTESPT) for increased crosslinking and trisilanol (heptaisooctyl) polyhedral oligomeric silsesquioxane (TS-iOc₇-POSS) for increased hydrophobicity. The prepared sols were deposited on aluminium alloy AA 2024-T3 and electronic boards. The coatings on AA 2024-T3 were used for potentiodynamic characterisation and for SEM and atomic force microscopy (AFM) characterisation of the surface. Raman spectroscopic measurements showed the suitability of the method for analysis of PDMSTU/BTESPT/TS-iOc₇-POSS based coatings on AA 2024-T3 and also was suitable

for detection of deposited coating on the electronic boards. Electronic boards represent a challenging substrate for coating deposition because of an uneven surface, tips and different substances present on them, for example metals, alloys and different polymers. The ability of confocal Raman spectroscopy to detect the coating under these conditions and its non destructive nature make it an ideal tool for the control of surface coverage on difficult substrates.

Key words: sol-gel, IR, Raman, PDMSTU, corrosion, organic-inorganic nancomposites, thin sol-gel coating