



Synergistic Protection against Corrosion of AA2024-T3 by Sol-Gel Coating Modified with La and Mo-Enriched Zeolites

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The present work demonstrates an improvement in corrosion protection of sol-gel coatings modified with a mixture of lanthanum and molybdate-enriched zeolite microparticles (La+Mo) due to synergistic effect between lanthanum and molybdate. The effect of these inhibitor species on protection of AA2024-T3 substrate has been studied by Electrochemical Impedance Spectroscopy and Localized Electrochemical Impedance Spectroscopy. Both techniques revealed an enhanced protection when compared with the case where the inhibitors were used alone. The inhibiting mechanism could involve on demand release of molybdate and lanthanum ions from the loaded zeolite followed by the formation of molybdenum oxide/hydroxide and a Mo-Na-La compound on intermetallic particles.

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Manuscript submitted November 19, 2013; revised manuscript received February 4, 2014. Published February 19, 2014.

One of the most common strategies used by corrosion engineers to protect metallic structures against corrosion degradation is the application of protective coatings. Organic coating systems have been widely used and consist of several "coating" layers where each one has a specific action. Hybrid sol-gel films have been extensively studied during the last decade as a possible pre-treatment/primer layer^{1,2} for different materials and alloys and used as model matrix for different encapsulated corrosion inhibitors.³⁻¹⁰ However, these films have low thickness and do not provide a suitable barrier effect. Formation of cracks or other type of defects initiate a more pronounced disruption of the barrier properties leading to corrosion.^{2,3} In order to provide the desirable protection performance of sol-gel coatings, the addition of corrosion inhibitors (such as cerium or lanthanum)^{11,12} is necessary.¹³ However, the simplest way of introduction of the inhibiting species, direct addition to the sol-gel formulation, proved to be unsuitable for high concentration of the species due to interaction with the film matrix leading to an early destruction of the barrier effect.¹⁴ For example, the protection of sol-gel film doped with $\text{Ce}(\text{NO}_3)_3$ is only observed if the amount of Ce^{3+} is in the 0.2 to 0.6 wt% range.¹⁴ Alternative approaches with encapsulation of inhibitors in nano-/micro-containers^{3-10,15-17} have been tried to enhance the protection properties of the sol-gel coatings without disrupting the barrier effect of the film. Among these, one successful approach has been the use of zeolite microparticles loaded with inhibitor species.^{7,9,10} Considerable improvement of protective performance has been achieved in sol-gel coatings modified with a mixture of cerium and molybdate-enriched zeolite microparticles (Ce+Mo coating)¹⁰ and a sol-gel modified with cerium-enriched zeolite (Ce-NaX coating).^{7,9} Experimental evidence showed that there is a controlled release of cerium and molybdate ions, in response to the adsorption of Mg^{2+} ¹⁰ and Cu^{2+} ⁹ by ion-exchange reactions, followed by their precipitation on intermetallic (IM) particles^{9,10} slowing down the corrosion activity. In fact, the significant improvement observed on protection performance with Ce+Mo coating was due to a synergistic effect between the two species released on demand from the loaded zeolites. Otherwise it would not be possible to accomplish the formation of a stable molybdenum containing-oxide/hydroxide film on the IM particles and the behavior of this coating would be similar to the sol-gel film modified only with Mo-enriched zeolite only or Ce-enriched zeolite.¹⁰ Experimental evidence also showed that zeolite-enriched microparticles have the ability to adsorb Cl^- ions from the electrolyte solution.⁹

The aim of this work is to exploit possible synergistic effect between lanthanum and molybdate and their respective inhibiting mechanisms in sol-gel modified with a mixture of lanthanum and

molybdenum-enriched zeolite microparticles. The enriched-zeolite microparticles were characterized by energy-dispersive X-ray fluorescence technique (EDXRF) and X-ray diffraction (XRD). Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) was also used to characterize the zeolite microparticles, the surface and cross-section of the developed sol-gel coatings modified with the zeolite microparticles before and after the electrochemical tests. The protection performance was assessed by electrochemical impedance spectroscopy (EIS) and localized electrochemical impedance spectroscopy (LEIS) measurements. The release of La and Mo-containing species from inhibitor enriched-zeolite microparticles was studied by EDXRF and atomic absorption spectrometry (AAS).

Experimental

Materials.— AA2024-T3 aluminum alloy plates were used in this study as metallic substrate. All panels were chemically etched before application of the coatings. An industrial-like three-step cleaning procedure consisting of alkaline cleaning in Metaclean T2001 at $60 \pm 10^\circ\text{C}$ for 18 min, followed by alkaline etching in P3 Almeico at $30 \pm 10^\circ\text{C}$ for 3 min and then acid etching in Turco Liquid Smutgo NC at $30 \pm 5^\circ\text{C}$ for 3 min. Finally the panels were rinsed with distilled water.⁷

Zeolite microparticles (NaX) were obtained from Sigma-Aldrich (Ref. 283592, $\text{Na}_x\text{Al}_{58}\text{Si}_{134}\text{O}_{384} \cdot z\text{H}_2\text{O}$, 13X). The Si/Al molar ratio of the particles was 1.23 and the average particle size $< 2 \mu\text{m}$. Lanthanum-enriched zeolite microparticles (LaNaX) were prepared by ion-exchange reaction of NaX with 0.1 M solution of lanthanum (III) nitrate hexahydrate (Sigma-Aldrich, 99.999%). The reaction took place in NaNO_3 solution (NaOH of Riedel deHaën, analytical reagent and HNO_3 of Riedel deHaën, min. 65%) with a volume/solid ratio (V/P) = 20 (in mL/g) at 80°C for 3 h. Then, the microparticles were filtered, washed with de-ionized water (in a volume five times higher than the volume of the solution used for ion-exchange) and dried during 10 hours at 100°C in an oven (Heraeus, model UT-5042). The La concentration in the LaNaX zeolite microparticles was determined by EDXRF. The crystalline structure of the ion-exchanged powders was controlled by XRD.

Molybdate-enriched zeolite microparticles (MoNaX) were prepared by incipient impregnation of NaX zeolite microparticles with 0.1 M solution of ammonium heptamolybdenum ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) as reported in.¹⁰ The reaction took place in NaNO_3 solution with a volume/solid ratio (V/P) = 1.5 (in mL/g) at room temperature during 24 h. Then, the microparticles were filtered, washed with de-ionized water (in a volume five times the volume of the solution used for ion-exchange) and dried during 10 hours.

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