

# Efficient lanthanum sol-gel thin films for corrosion protection

Manuel Abuín<sup>1</sup>, Aida Serrano<sup>2</sup>, José Llopis<sup>1</sup>, Miguel-Ángel García García-Tuñón<sup>2</sup> and Noemí Carmona<sup>1\*</sup>

<sup>1</sup> Department of Materials Physics, Complutense University of Madrid, Madrid 28040 Spain

<sup>2</sup> Glass and Ceramic Institute, CSIC, Madrid 28049, Spain

## KEYWORDS

Lanthanum; corrosion protection; sol-gel coating; atomic force microscopy; X-ray absorption spectroscopy

\* Corresponding author E-mail: n.carmona@fis.ucm.es

## ABSTRACT

Anticorrosive silica films doped with lanthanum ions were synthesized by the sol-gel method as an alternative to chromate (VI)-based conversion coatings. Simulated corrosion tests in acid and basic media showed their effectiveness for the corrosion protection of aluminum alloy and suggest an environmentally friendly low cost processing hybrid barrier coating.

This work presents a low cost environmentally friendly alternative to corrosion protection of aluminum alloy based on silica sol-gel thin films doped with lanthanum ions. Films show comparable properties with previous ones found in literature and fulfill modified ISO standards for corrosion resistance.

Corrosion of metallic structures has significant impact on countries economy and a big effort is made every year to provide strategies to minimize the impact of corrosion. Recent legislation according to anti-corrosive pre-treatments based on chromates has motivated the increase of the corrosion protection industry. The use of Cr (VI) as anti-corrosive pre-treatment for metallic surfaces is becoming increasingly restrictive due to its carcinogenic characteristic for the human race and substantial contribution to environmental pollution.

One of the most successful alternatives for obtaining thin films with improved properties is sol-gel technology. It represents a more environmentally friendly surface treatment that combine several functions as high transparency in the VIS region, good adhesion, hydrophobic character, good chemical and mechanical resistance (<sup>1</sup>, <sup>2</sup>).

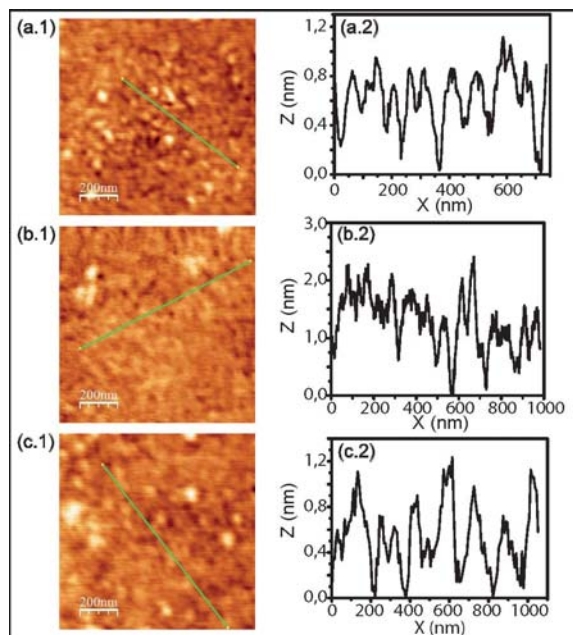
Additionally to the development of protective films with desired properties for the industry, the transfer to market of affordable coatings is also critical.

Rare earth metals, as lanthanum, are effective ions in slow down the corrosion rate of cathodic reaction precipitating as oxides to form a passivation-protective layer on the metal. Furthermore, it is expected that the addition of lanthanum ions in protective films would have good self-healing properties, as the chromates have.

For the synthesis of the protective films, solutions composed of TEOS (tetraethylorthosilicate) and MTEOS (methyl-triethoxysilane) were prepared. Distilled water was added to perform the hydrolysis, absolute ethanol was used as solvent and nitric acid as catalyst. The respective molar ratios were 0.8 : 0.2 : 3 : 8 : 0.01. La(III) acetate hydrate was added in 1 mol % as doping agent. For comparison purposes only, films with La(III) isopropoxide were also prepared. To overcome the limitation due to the expensiveness of this compound, the alternative compound, La(III) acetate hydrate, will be preferred. Solutions were stirred for 2 h before deposition. Aluminum alloy AA2024-T3 sheets were used as substrates and films were deposited by dip coating at room temperature (25 °C) and relative humidity (35 %). After coating, samples were dried and annealed in air at 500 °C.

Films resistance against corrosion was checked by weathering tests according to a modification of ISO 1770 and 695 standards (<sup>3</sup>, <sup>4</sup>), in order to adapt them to thin films evaluation. Samples were immersed into an acid solution (HCl 0.1N at 25 °C) or into a basic one (NaOH 0.1N at 25 °C) for 1 hour.

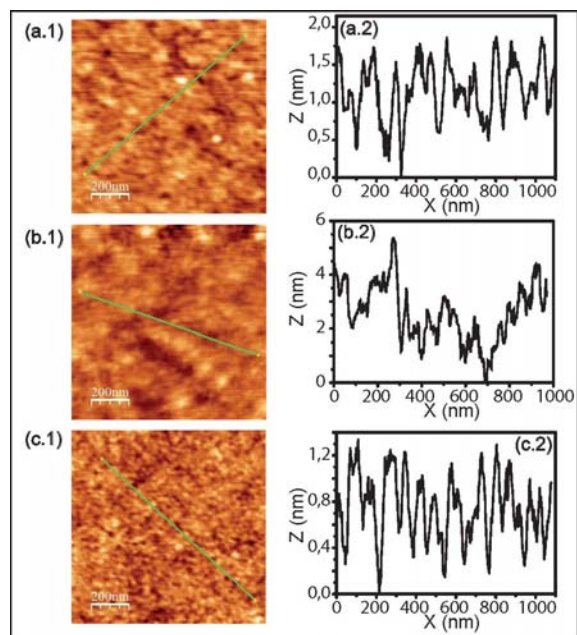
Morphology and roughness of the surfaces of prepared silica sol-gel films doped with La (III) ions before and after the attacks have been performed by Atomic Force Microscopy (AFM) (Fig. 1). Films from the acetate precursor reveal a surface roughness (root mean square, RMS) value of  $0.37 \pm 0.01$  nm for the film without weathering,  $0.48 \pm 0.01$  nm for the film after acid attack and  $0.61 \pm 0.01$  nm after basic attack. This indicates an almost no alteration of the surface (It is below 1 nm deep). The cross-section profiles drawn for each image reveal well preserved irregular shapes.



**Figure 1.** AFM topography image of a La (III) sol-gel film from the acetate precursor: surface a.1) without weathering, b.1) after basic attack, and c.1) after acid attack. a.2), b.2) and c.2) AFM cross-section profiles of the respective films.

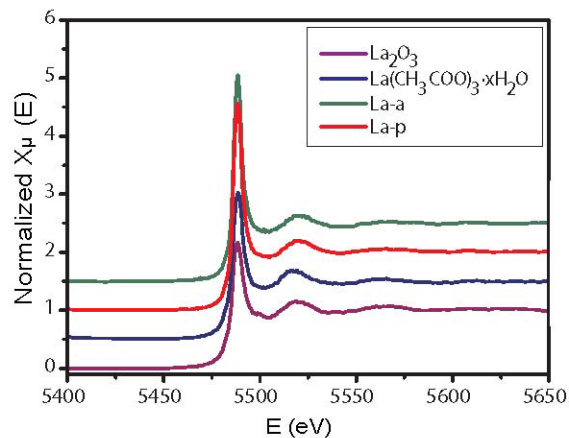
Figure 2 displays the AFM topography images of the silica films prepared from the La (III) isopropoxide. RMS values are:  $0.42 \pm 0.01$  nm for the reference films without treatment,  $0.98 \pm 0.01$  nm for films after basic attack, and  $0.33 \pm 0.01$  nm for films after acid attack. Superficial features in these films also are formed by irregular structures with sizes down to 1 nm deep. This confirms well preservation against corrosion also for films prepared from the propoxide precursor.

Optical analysis of the La films showed colorless, homogeneous and crack-free surfaces well adhered to the substrates. They presented high transparency in the VIS range (400-700 nm) with transmittances above 90 %, regardless from the precursor used (acetate or isopropoxide). The wavelength of UV cut-off at 50 % transmittance for the films prepared from the acetate was 301 nm and films thickness was around  $233 \pm 16$  nm. Coating thickness after acid attack increased up to  $295 \pm 5$  nm, which may indicate a self-repairing mechanism with  $\text{La}(\text{OH})_3$  formation (the AFM topography analysis shows the least RMS value); and after basic attack thickness diminished until  $271 \pm 7$  nm, which confirms film resistance against corrosion. The corresponding values for the films prepared from the isopropoxide precursor show a coating thickness of  $205 \pm 13$  nm before weathering, an increase of the thickness after the acid attack up to  $278 \pm 5$  nm, and a wide decrease after the basic attack ( $90 \pm 50$  nm). These results indicate, in general, a better behavior against both attacks for the silica doped with lanthanum acetate films.



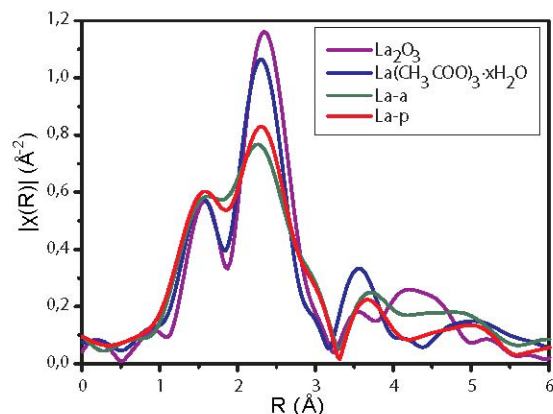
**Figure 2.** AFM topography image of a La (III) sol-gel film from the isopropoxide precursor: surface a.1) without weathering, b.1) after basic attack, and c.1) after acid attack. a.2), b.2) and c.2) AFM cross-section profiles of the respective films.

La isopropoxide is an alcoxide as well as TEOS. It suffers hydrolysis and polycondensation during the gel formation. However, La acetate hydrate is an affordable more economical soluble salt. The location of La(III) ions in the final film structure is not known certainly and may differ depending on the precursor used in the synthesis. To elucidate this, the  $L_3$ -edge XANES spectra of the films prepared from La acetate and La isopropoxide and reference compounds  $\text{La}_2\text{O}_3$  and  $\text{La}(\text{Ac})_3$  have been registered. The position of the absorption edge (Fig. 3) appears at ca. 5489 eV and does not change with the precursor used, indicating no change in the oxidation state of  $\text{La}^{3+}$  ions. It also does not change after the accelerated corrosion tests.



**Figure 3.**  $L_3$ -edge XANES spectra of the films prepared from La acetate (La-a) and La isopropoxide (La-p) and the reference compounds  $\text{La}_2\text{O}_3$  and  $\text{La}(\text{Ac})_3$ . Curves have been vertically displaced for clarity.

The post-edge region of the spectrum beyond the  $L_3$  edge, named the Extended X-ray Absorption Fine Structure (EXAFS), provides information about bond distances and coordination numbers. In our prepared films, according to <sup>(5)</sup>, calculated data La-O bond distance for a  $\text{La}^{3+}$  ions with a coordination number of 6 is 2.43 Å, versus an experimental La-O distance found of ca.  $2.4 \pm 0.1$  Å (Fig. 4). EXAFS spectra of the reference compounds ( $\text{La}_2\text{O}_3$  and  $\text{La}(\text{Ac})_3$ ) show similar interatomic La-O distance (ca.  $2.4 \pm 0.1$  Å). At around  $3.8 \pm 0.1$  Å we find the second  $\text{La}^{3+}$  neighbor,  $\text{Si}^{4+}$ , also identified by <sup>(6)</sup> and considered as  $\text{La}^{3+}$  ions in silicate sites. The theoretical calculated La-O-Si bond distance is 3.89 Å. These results confirm the incorporation of  $\text{La}^{3+}$  ions in silicate sites inside the films prepared (both from acetate and propoxide precursors).



**Figure 4.**  $L_3$ -edge EXAFS spectra of the films prepared from La acetate and La isopropoxide and the reference compounds  $\text{La}_2\text{O}_3$  and  $\text{La}(\text{Ac})_3$

It is interesting to mention that the addition of even 1 mol % of  $\text{La}^{3+}$  ions could bring about this considerable improvement in the films properties, demonstrated by the AFM and XAS analyses performed.

In summary, we may indicate the convenience and effectiveness of the prepared sol-gel silica films doped with 1 mol % of lanthanum acetate as a protective barrier for the delay of early corrosion of metallic surfaces. Lanthanum acetate is an affordable chemical reactive able to be employed as dopant in industrial processes, that is why we present here a real alternative that opens many possibilities for an environmentally friendly low cost processing sol-gel hybrid films for the replacement of chromate (VI) pretreatments on metals.

**Acknowledgment.** The authors are pleased to thank the XAS Beamline BM25 (Spanish-SP line CRG) at the European Synchrotron Radiation Facility, ESRF (Grenoble, France) and especially to Dr. J.A. Gallastegui and Prof. G.R. Castro for their assistance during the XAS experiments. The financial support of the FSE-MEC, Ramon y Cajal program ref. RYC-2007-01715 is also acknowledged.

<sup>1</sup> E.V. Skorb, A.G. Skirtach, D.V. Sviridov, D.G. Shchukin, H. Möhwald, Laser-controlable coatings for corrosion protection, ACS Nano 3 (2009) 1753-1760.

<sup>2</sup> G. Schottner, Hybrid sol-gel derived polymers: applications of multifunctional materials, Chem. Mater. 13 (2001) 3422-3435.

<sup>3</sup> ISO 1776, Glass. Resistance to Attack by Hydrolytic Acid at 100 Degrees C. Flame Emission of Flame Atomic Absorption, 1985.

<sup>4</sup> ISO 695, Glass. Resistance to Attack by a Boiling Aqueous Solution of Mixed Alkali. Method of Test and Classification, 1975.

<sup>5</sup> D.R. Lide, CRG Handbook of chemistry and physics, 89th Ed, 2008, Taylor & Francis Group, New York.

<sup>6</sup> P. Jollivet, C.D. Auwer, J.M. Delaye, E. Simoni, Evolution of the local environment of lanthanum during simplified SON68 glass leaching, J. Non Cryst. Solids 353 (2007) 344-353.