SIO₂ MESOPOROUS THIN FILMS AS NANOCONTAINERS FOR CORROSION INHIBITORS IN SELF-HEALING ANTICORROSION COATINGS
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ABSTRACT

Among the different alternative surface treatments developed in view of the coming prohibition of chromates in aeronautic applications, sol-gel coatings show very promising properties. These layers provide a barrier against aggressive environments. Moreover, their performance can be improved by introducing inhibitive agents in the coating. However, the direct introduction of corrosion inhibitors in the sol-gel compromises their barrier properties. Nanocontainers are consequently used for the storage of inhibitive agents and dispersed in the sol-gel matrix to avoid direct interactions between components. In case of scratch or when stimulated by external action, nanocontainers release active compounds which form a protective layer healing the defect.

In this work, a mesoporous sol-gel thin film synthesized through “Evaporation Induced Self Assembly” process was used as nanocontainer for 2024 aluminium protection. The mesoporosity developed through the layer was employed to host organic corrosion inhibitors inside the film and consequently to offer an active corrosion protection.

Morphology of the layer was characterized using transmission electron microscopy (TEM) and adsorption porosimetry. High specific surface area and well-organized pores are obtained, providing high-load ability for active species. Incorporation of corrosion inhibitors in the mesoporosity was checked using qualitative and quantitative analyses. Kinetics of active agents release was studied by UV/visible spectroscopy. Successful incorporation in the sol-gel matrix and possible release of corrosion inhibitors were observed. The self-healing properties were underlined by immersion test in aggressive sodium chloride solution.

1. INTRODUCTION

Sol-gel coatings have attracted much attention in the field of anticorrosive protective layers for 2024 aluminum alloys since they are able to offer efficient barrier against aggressive corrosive species. A lot of researches also aim at improving sol-gel coatings performance by introducing corrosion inhibitors inside the matrix. The idea is to benefit from their local protection to heal the sol-gel film in case of damage. Different means can be used to incorporate corrosion inhibitors. The active agent can be directly added into the silica network during the synthesis, which is a very attractive route as the material can then be processed in one step. However, the solubility of the compound in the sol may limit the amount of inhibitor. Another problem is that the active compound can interfere with the hydrolysis and
condensation reactions, modify the final sol-gel properties and reduce the inhibitor efficiency. As the result, barrier properties of the sol-gel film are weakened by direct addition [1]. Other means of loading include the use of intermediate nanocontainers, such as nanoclays or polyelectrolytes, which are themselves dispersed in the sol. However, with this latter method, it is difficult to ensure a homogeneous dispersion of the active compound and a good compatibility within the matrix.

In this work, in order to overcome these problems, incorporation of corrosion inhibitors was achieved by adsorption onto a silica mesoporous sol-gel thin film. In this way, amount of active agent is only limited by the porous volume of the film and the compound is available in case of corrosion processes. The use of the direct inner porosity of the layer also allows avoiding dispersion and compatibility problems observed with intermediate nanocontainers.

2. MATERIALS AND METHODS

2.1. Synthesis of the mesoporous film and characterization

Mesoporous films were synthesized through “Evaporation Induced Self-Assembly” process using P123 block copolymer from Pluronic family as templating agent, ethanol as solvent and tetraorthosilicate (TEOS) as precursor. In molar ratio, the composition of the sol was 1 TEOS: 0.005 P123: 6 H2O: 0.001 HCl: 9 EtOH. Films were prepared by dip coating with a withdrawal rate fixed at 60 mm/min and aged under controlled atmosphere (70% RH and 25°C) during 24 h to get reproducible mesoporous structures. Synthesis was inspired by work of Alberius and al. [2] to get a cubic structure which provides more accessible porosity from the surface. Polished silicon substrates and quartz resonator were used according to characterization techniques (respectively, TEM imaging and adsorption porosimetry). After ageing, the film mesostructure was stabilized at 150°C during 30 min and then treated under UV/ozone illumination to remove P123 and create mesoporosity. Elimination of the templating agent is generally achieved by calcination step at temperature higher than 250°C but this process was here avoided due to its incompatibility with aluminum substrates.

Mesoporous films were characterized by transmission electron microscopy (TEM) and adsorption porosimetry based on quartz crystal microbalance analyser (QCM). The principle consists in using a QCM to measure water vapor adsorption and desorption quantities for different water partial pressures. QCM is indeed able to accurately detect very tiny mass changes (about 10^{-8} g/Hz) by measuring variations of frequency. These adsorption and desorption isotherms provide characteristics of the pore network.

2.2. Corrosion inhibitor loading

Mesoporous films were immersed in a highly concentrated benzotriazole (BTA) solution (20g/l in ethanol) for 24 h at room temperature. Films were then dried in a desiccator to remove solvent from the porosity. Presence of BTA within the film was checked through adsorption porosimetry. Molecules adsorbed on pore surface indeed decrease the volume accessible for water vapor. UV/visible absorption spectroscopy was also used to quantify the amount of active agent loaded inside the
film. All these analyses were performed before and after wiping off the surface with ethanol to differentiate molecules adsorbed on the film surface and inside the porosity.

2.3. Corrosive tests

2024 aluminum alloy panels were degreased in a commercial bath of TURCO® 4215™ NC-LT and the same procedure of mesoporous sol-gel deposition (see section 2.1.) was achieved on these substrates. However, for this test, a second sol-gel layer was added on the mesoporous thin film to heal the entrance of pores and avoid the direct release of BTA in the aggressive environment. Samples covered in this way were immersed in 0.05 M NaCl for several days and evolution of corrosion was observed.

3. RESULTS AND DISCUSSION

Mesoporous films present high optical quality and homogeneous thickness (about 300 nm). As observed in TEM images (Figure 1), the film structure is still present after UV/ozone treatment showing that the silica matrix does not collapse when P123 leaves the film. Pores are well-ordered and their size is comprised between 5 and 7 nm in agreement with previous work [2].

![Figure 1: TEM images of mesostructured film before UV/ozone treatment (left) and mesoporous film after UV/ozone treatment (right).](image)

Adsorption porosimetry was also achieved to get more information on accessibility to porous structure.

![Figure 2: Adsorption and desorption isotherms of water vapor on mesostructured and mesoporous films](image)

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Adsorption and desorption isotherms are superimposed for the mesostructured film (Figure 2). The P123 is still present in the porosity and the amount of adsorbed water is low. In opposition, for the film treated under UV/ozone, a hysteresis loop appears due to the capillary condensation of water inside mesopores. Films treated under UV/ozone illumination present high surface specific area and high pore volume. Moreover, this treatment does not affect mechanical properties of 2024 aluminium substrates [3].

Adsorption porosimetry was also used to estimate the loading efficiency by observing variations in water uptake and in total open pore volume (Figure 3). Just after loading, mesoporosity is no longer accessible for water molecules due to the presence of benzotriazole crystals on the film surface. After the wiping step, these molecules are removed and a reduction of the porosity can be observed in comparison with the mesoporous film. This decrease can be assigned to the adsorbed BTA molecules on the surface of mesopores. The hysteresis loop is also slightly shifted towards higher water relative pressure due to the hydrophobicity provided by BTA molecules.

Figure 3: Variations of water uptake during adsorption and desorption isotherms according to the presence of inhibitive molecules inside the porosity

Two different techniques were used to determine the BTA loading capacity of the mesoporous film (Table 1).

<table>
<thead>
<tr>
<th>QCM analyser</th>
<th>UV/visible</th>
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<tbody>
<tr>
<td>mg (BTA)/ g (film)</td>
<td>mol (BTA)/ cm² (film)</td>
</tr>
<tr>
<td>Total (before wiping)</td>
<td>846</td>
</tr>
<tr>
<td>In pore (after wiping)</td>
<td>142</td>
</tr>
</tbody>
</table>

Variations in frequency measured by the QCM analyzer before and after immersion in the inhibitive solution were converted into BTA mass uptake. Impregnated mesoporous films were also immerged in distilled water at neutral pH (volume of 20 ml) for several days to obtain the complete release of BTA. UV absorption of the
solution at 256 nm (maximum of absorption of the molecule) was converted into BTA concentration. These values were compared with the theoretical maximum loading capacity of the film (3.10^{-7} \text{ mol BTA/cm}^2 \text{ film}), assuming that all the pores are completely filled with benzotriazole molecules (molar volume 87.6 \text{ cm}^3/\text{mol}). The experimental loading is approximately one-third of the theoretical loading.

Finally, the benefit of BTA incorporation inside the film was highlighted by samples immersion in aggressive environment. Photographs taken after 7 days of immersion show the inhibiting effect of loaded mesoporous films when compared with empty films or bare aluminum. In presence of BTA, the surface only presents some pits while a considerable amount of pits and white deposits are observed for non impregnated films and bare aluminum.

![Photographs of samples immerged in NaCl 0.05M during 7 days; bare 2024 AA (left), 2024 AA covered with non impregnated mesoporous film (center) and 2024 AA covered with mesoporous film loaded with BTA (right).]

4. CONCLUSIONS

SiO$_2$ mesoporous films were synthesized and incorporation of BTA was possible into the porosity. Mesostructure is regular, reproducible and present cubic arrangement. Pores are consequently accessible from the film surface. The choice of P123 as templating agent allows getting pore size (6 nm) compatible with the dimension of BTA molecules (diameter 0.6 nm). The loading content of BTA was found to be 14% in weight and reaches 30% of the theoretical maximum loading. First corrosion tests achieved with a second sol-gel layer to seal the entrance of pores are very promising in terms of self-healing behaviour. However, it would be interesting to create stronger interactions between active compound and silica matrix to avoid direct release in the solution and to obtain pH-controlled release.

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