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EFFECT OF THE METALLIC CLEANING AND OXIDIZING PRE-TREATMENTS ON THE CORROSION BEHAVIOUR OF SOL-GEL HYBRID COATED EN AW-6063 ALLOY

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Abstract
The effect of alloy surface pre-treatments on the corrosion behaviour of sol gel hybrid coated EN AW 6063 alloy was studied. Five pre-treatments were used: solvent degreasing; alkaline degreasing followed by acid etching; alkaline degreasing followed by alkaline plus acid etching, alkaline degreasing followed by acid etching and oxide growth in boiling water and alkaline degreasing followed by acid etching and anodization. Surface morphology depends on the pre-treatment: SEM/EDS analysis revealed that alkaline plus acid cleaned samples exhibited a very smooth deoxidized surface, while all the others showed a rougher surface covered with an oxide layer. This oxide layer is denser and more homogeneous in the samples subjected to the oxide growth steps. A hybrid sol-gel coating, synthesized from glycidoxypropyltrimethoxysilane (GPTMS) and zirconium n-propoxide (TPOZ) precursors, was applied to the different pre-treated metallic substrate by dip-coating. The corrosion behaviour of the coated samples was evaluated by electrochemical impedance spectroscopy (EIS) and by an accelerated corrosion test. Complementarily to the corrosion study, the adhesion of the hybrid sol-gel coating was evaluated by cross-cut and bend tests. The corrosion tests revealed that the pre-treatments including the oxide growth steps lead to the best protection performance, followed by the alkaline degreasing and alkaline plus acid etching one. However, the latter exhibits the worst adhesive behaviour, attributed to the smoother and deoxidized surface of the substrate.

Keywords: Hybrid Sol-Gel Coatings, Pre-treatment, Anodization, Corrosion, Aluminium

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INFLUÊNCIA DOS PRÉ-TRATAMENTOS DE LIMPEZA E DE OXIDAÇÃO DA SUPERFÍCIE METÁLICA NO DESEMPENHO À CORROSÃO DA LIGA DE ALUMÍNIO EN AW-6063 COM REVESTIMENTO HÍBRIDO DE SOL-GEL

Resumo
O presente trabalho teve como objetivo o estudo da influência dos pré-tratamentos de superfície no desempenho à corrosão dos revestimentos híbridos de sol-gel para a proteção da liga de alumínio EN AW-6063. Para esse efeito foram adotados cinco pré-tratamentos: desengorduramento com acetona, desengorduramento alcalino seguido de ataque ácido, desengorduramento alcalino seguido de ataque alcalino e ataque ácido, desengorduramento alcalino seguido de ataque ácido e imersão em água à temperatura de ebulição e desengorduramento alcalino seguido de ataque ácido e anodização. A morfologia e a composição química da superfície dependem do tipo de pré-tratamento aplicado. As análises SEM/EDS realizadas revelaram que as amostras sujeitas a ataque químico alcalino seguido do ácido apresentam uma superfície mais lisa e desoxidada. Todos os outros pré-tratamentos deram origem a superfícies mais rugosas, cobertas com uma camada de óxido, mais denso e homogéneo nas amostras sujeitas aos passos adicionais de crescimento do óxido.
Os revestimentos híbridos de sol-gel, sintetizados a partir dos precursores glicidoxipropiltrimetoxissilano (GPTMS) e n-propóxido de zircónio (TPOZ), foram aplicados nos diferentes substratos metálicos pré-tratados por imersão (dip-coating). O comportamento à corrosão das amostras revestidas foi avaliado por espectroscopia de impedância eletroquímica (EIS) e por um ensaio de corrosão acelerada. Complementarmente aos ensaios de corrosão, foram realizados ensaios de aderência do revestimento híbrido de sol-gel usando os métodos da quadrícula e de dobragem. Os ensaios de corrosão revelaram que os pré tratamentos que incluíam os passos de espessamento da camada de óxido conduziram ao melhor desempenho anticorrosivo, seguidos pelo tratamento que envolveu os ataques alcalino e ácido. No entanto, este último exibiu o pior desempenho no que se refere à aderência do revestimento sol-gel ao substrato metálico, o que foi atribuído à menor rugosidade e reduzida oxidação da superfície deste.

Palavras-chave: Revestimentos Híbridos de Sol-Gel, Pré-tratamento, Anodização, Corrosão, Alumínio

1. INTRODUCTION

The 6000 series aluminium alloys (Al-Mg-Si) offer an unique combination of properties such as good corrosion resistance (in mild corrosive environments), due to the spontaneous oxide layer formed on their surface, good mechanical resistance and design flexibility, which makes them widely used in the construction industry. This type of alloys, however, develops pitting in marine highly polluted environments. Thus, to fulfil long term service life requirements and reduce maintenance, aluminium-based building components are often organically coated what requires alloy surface pre-treatment and a conversion layer (often based on Cr(VI)) to improve adhesion.
The organic-inorganic hybrid silane based sol-gel coatings have proved to be a promising environmentally friendly alternative to Cr(VI) conversion layers, exhibiting barrier effect, ability to incorporate corrosion inhibitors and compatibility with organic coatings [1]. To be effective as conversion layer substitute, the hybrid sol-gel coatings should also adhere properly to the substrate, what is achieved by the establishment of chemical bonds such as Al–O–Si [1,2] with the alloy, through the hydrolysis and condensation reactions involved in the

sol-gel film formation process. In this context, the pre-treatment of the surface plays an important role in the corrosion resistance of sol-gel coated alloy. Besides removing surface contaminants and intermetallic compounds prone to develop pitting, it also provides a clean surface where a more homogenous native oxide is formed to which the sol gel film will attach [3].

The influence of the metallic surface treatment in the corrosion resistance of sol-gel coated alloy has been studied by several authors, with somewhat divergent results. Feng *et al.* [4] reported that acid etching of AA2024-T3 prior application of the sol-gel coating improves its corrosion performance relatively to alkaline plus acid etched coated specimens. Alvarez *et al*. [3] found that the solvent degreased samples yielded better corrosion resistance than those only polished or alkaline degreased followed by alkaline plus acid etching treatments, what was attributed to the good barrier properties of the native oxide. Hamdy [5] found that this oxide thickening through a double step surface pre-treatment involving alkaline etching and immersion in boiling water enhanced the corrosion resistance of sol-gel ceria coated AA6061-T6 samples in comparison to the single step treated ones, while those coatings applied on only solvent degreased samples could not offer good corrosion protection. Recently, several authors [6-8] studied the effect of combining anodization with silane based sol-gel coatings to improve the corrosion protection of magnesium and aluminium alloys. Their findings demonstrated that anodizing plus sol-gel coating provided superior corrosion resistance compared to the equivalent non anodized silane coated samples or to the solely anodized, demonstrating a synergistic effect resultant from this double step pre-treatment [6].

In this work, to study the effect of surface pre-treatments on the corrosion behaviour of a sol-gel coated EN AW 6063 alloy, four different types of pre-treatment were applied, comprising: solvent degreasing; alkaline degreasing followed by alkaline or acid etching or both, alkaline degreasing followed by acid etching and oxide thickening in boiling water. To further evaluate the benefits of this oxide layer growth on the improvement of corrosion resistance, a fifth pre-treatment involving anodizing in sulphuric acid after alkaline degreasing and acid etching was also included. This corrosion study was complemented by the evaluation of the hybrid sol-gel coating adhesion by the cross-cut and bend tests.

2. MATERIALS AND METHODS

2.1 Aluminium surface pre-treatment and sol-gel coating synthesis

EN AW 6063 alloy samples of 3.5 cm × 7 cm, 1 mm thick sheet, were abraded to 1000 finish with SiC grit papers, washed in deionised water, ethanol and dried. Prior to sol-gel coating the following surface pre-treatments were applied:

(a) solvent degreasing (D): samples were cleaned by acetone wiping;
(b) alkaline degreasing followed by acid etching (AC): first samples were cleaned in an aqueous solution of P3 Almeco 18C (Henkel) for 10 min at 60 °C, followed by immersion in HNO_3 (20 %) for 15 min at room temperature;
(c) alkaline degreasing followed by alkaline plus acid etching (AAC): first samples were cleaned in an aqueous solution of P3 Almeco 18C (Henkel) for 10 min at 60 °C, followed by immersion in 0.05 M NaOH solution for 5 min at room temperature and then immersed in HNO_3 (20 %) for 5 min at 45 °C;
(d) alkaline degreasing followed by acid etching and oxide growth (ACO): treatment described in (b) followed by immersion in boiling water for 30 min;
(e) alkaline degreasing followed by acid etching and anodization (ANO): treatment described in (b) followed by immersion in a sulphuric acid solution containing 200 g/L of H_2SO_4 and 117 g/L of $Al_2(SO_4)_3.16H_2O$ (used as aluminium source). Anodization was performed at a constant current of 1.5 $A.dm^{-2}$ for 15 min at room temperature (20± 2) °C. The anodizing time chosen aimed to obtain an anodic oxide coating thickness of about 5 μm.

After each pre-treatment step, the samples were rinsed in desionised water and at the end of treatment further dried at 60 °C for 15 min in an oven. All samples were kept in the laboratory for one week prior to sol-gel coating application. The AC and AAC pre-treatments are based on industrial practice. The AAC pre-treatment parameters were targeted to achieve a mass loss of 2 g/m^2 [9], the AC pre-treatment mass loss is around one tenth of this value. The oxide growth step was adapted from literature [10] and the anodization conditions followed QUALANOD rules [11].

The hybrid coating was synthesized from glycidoxypropyltrimethoxysilane (GPTMS) and zirconium n-propoxide (TPOZ, 70 % in n-propanol) precursors, based in the procedure described in previous works [12,13], hydrolysed separately and mixed in a proportion to achieve 20 % of TPOZ in the final sol-gel solution. The sol-gel coating was applied to the different pre-treated aluminium alloy samples by dip-coating. After coating, the samples were dried at room temperature and cured at 130 °C in an oven for 1 hour.

2.2 Characterization techniques and testing methods

Surface observation and chemical elemental analysis were performed in a JEOL JSM-6400 scanning electron microscope with a EDS detector coupled (Inca-xSight, Oxford Instruments) (SEM/EDS). The corrosion behaviour of the coated samples was evaluated by electrochemical impedance spectroscopy (EIS) and by an accelerated corrosion test. EIS tests were performed in aerated NaCl 0.5 M solution with a Gamry Potentiostat REF600-06704, applying a 10 mV sinusoidal perturbation at the Open Circuit Potential, in the frequency range 100 kHz - 5 mHz. A three-electrode cell was used, with a SCE electrode as reference, a platinum wire as counter-electrode and the coated sample as working electrode. The accelerated corrosion test involved the exposure of scribed coated samples in a wet chamber (40 °C; 82 % RH) during 1000 h, after 1 min contact of the scribe with HCl (38 %). The coated samples were also subjected to cross-cutting (ISO 2409 [14]) before exposure and to bending (ISO 1519 [15]) after wet chamber exposure, to evaluate coating adhesion.

3. RESULTS AND DISCUSSION

3.1 Morphology of alloy surface after pre-treatment and coating

The surface of the AW-6063 samples subjected to the different pre-treatments was observed in the SEM. Fig. 1 shows the SEM micrographs obtained. The surface morphology of acid cleaned (AC) samples is very similar to that of the one only degreased (D) showing a low etch degree, but with cavities associated to the attack and removal of intermetallic compounds particles. The alkaline plus acid cleaned (AAC) samples exhibited an even more etched surface, very smooth and deoxidized. The samples subjected to the oxide growth step (ACO) and to anodization (ANO) exhibit a more homogenous and dense oxide layer covering the entire surface (including the intermetallic cavities) in comparison to the acid cleaned samples (AC).

After sol-gel coating, SEM observations revealed a very homogeneous, crack free surface for all samples, showing that the sol-gel coating covers uniformly all the substrate's surface, which became very smooth. These coatings practically do not show any irregularities, except in the case of the coated sample only previously degreased (D) in which surface some "pin-hole" type defects are perceptible. SEM-EDS analyses carried out inside these defects proved that they correspond to zones in which the sol-gel layer should be thinner than in the surrounding surface.

A cross-sectional SEM micrograph of a sol-gel coated aluminium alloy sample subjected to the anodization pre-treatment (ANO) is presented in Fig. 2. This image shows two layers corresponding to the sol-gel and the anodic oxide coatings covering continuously the alloy surface, without significant defects or cracks perceptible in depth. The anodic oxidation coating thickness measurements using an Eddy–current device (model A300 NP-3, ELCOMETER), carried out before sol-gel coating, indicate an average oxide coating thickness of ~5 µm, what is in good agreement with SEM observations. Using the SEM's equipment measuring tool, previously checked by a calibrated stage micrometer, several measurements of sol-gel coatings thickness were carried out at different points on samples cross-sections. From these measures is estimated that sol-gel coating thickness in the different pre-treated samples should range between 1.5 µm and 2.5 µm.

3.2 Corrosion behaviour of sol-gel coated samples

3.2.1 Electrochemical Impedance characterization

To evaluate the corrosion behaviour, hybrid sol-gel coated alloy samples were immersed in 0.5 M NaCl solution for 28 days. After this time, all samples except the one previously anodized showed localized corrosion of the substrate involving coating cracking and detachment. This localised corrosion was more intense and frequent in the coated sample only degreased (D), while the one treated with the additional oxide growth step (ACO) was the least damaged by corrosion, followed by the double etched one (AAC).

Fig. 3 shows the impedance spectra obtained after 1 hour and after 28 days of immersion, for the different pre-treated coated samples. Comparatively to all the others, the EIS spectra of the coated sample subjected to the anodization step show increased impedance values by about one order of magnitude or more, almost across all frequencies, demonstrating the superior corrosion resistance of this "duplex" coating system, during all immersion time in agreement with visual observation.

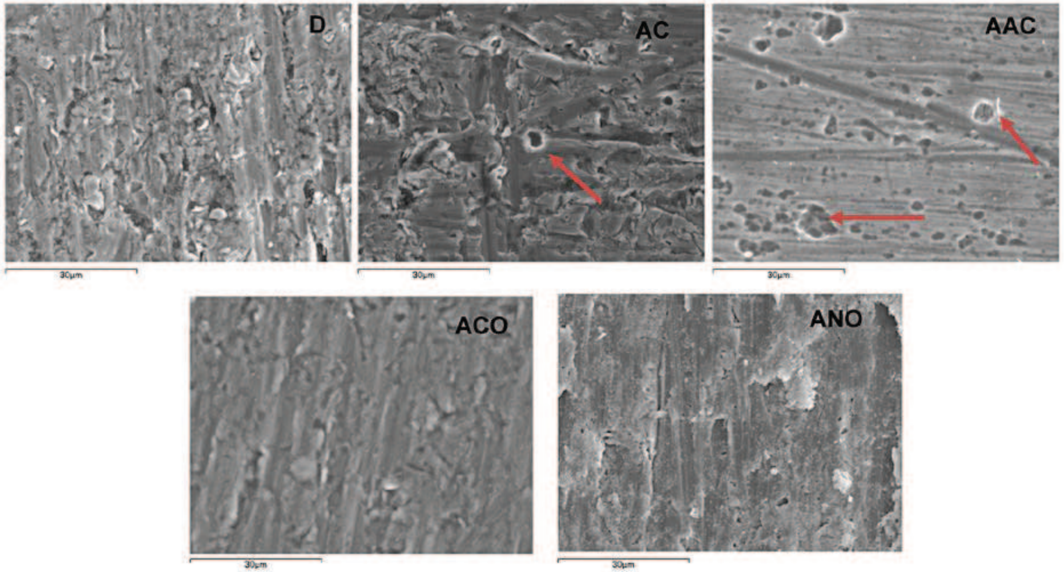

Fig. 1 - SEM micrographs of aluminium alloy samples surface after the different pre-treatments (arrows point to cavities left by intermetallic compounds particles removal).

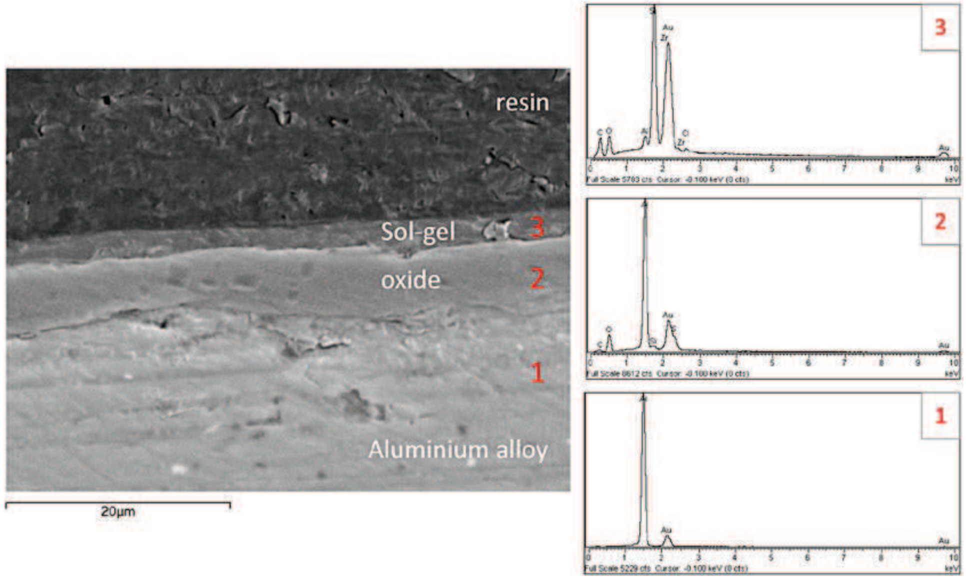

Fig. 2 - Cross sectional SEM micrograph of an anodized (ANO) pre-treated aluminium sample showing the double coating system and typical EDS spectra obtained in the signed zones. (The test specimen's surface was sputtered with gold to allow better electric contact).

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In the beginning of immersion (Fig. 3(a)), all EIS spectra depict two time constants that can be related to the sol-gel coating (at higher frequencies) and to the aluminium oxide layer present at the metal/coating interface (at lower frequencies) [13]. It should be noticed that for the anodized coated sample (ANO) it is assumed that this latter time constant derives solely from the anodic oxide porous layer contribution, since the barrier layer impedance response should be too large to be detected in the EIS measurements performed [8]. The resistive plateau observed in all spectra at medium-high frequencies range (10^5 Hz-10 Hz) is associated to the sol-gel coating barrier properties [13]. For the longer immersion time (28 days), all coated samples, except the anodized one, show a generalized decrease in impedance at this frequencies range and the high frequency time constant can hardly be distinguished. This behaviour indicates a marked decrease of the sol-gel coating barrier properties with time due to water penetration through its pores. The slight decrease in the impedance at the lower frequencies region (0.1 Hz-10^{-2} Hz) indicates a slight reduction of the oxide layer resistance with immersion time, especially in the case of D pre-treatment, in which EIS spectra a new time constant can be visualised at ~0.01 Hz, that can be ascribed to the onset of corrosion processes [13]. In relation to the anodized coated sample (ANO), the respective Bode plots obtained after 28 days of immersion in the 0.5 M NaCl solution (Fig. 3(b)) reveal an increase in the impedance values for the frequencies above 1 Hz and a lay-out typical of a sealed anodized coating [16], with the time constants associated to the inner barrier layer (at low frequencies) and to the outer porous layer (at high frequencies) . A possible explanation for this evolution is that due to the reduction of the sol-gel coating barrier properties, water penetrating through sol-gel pores reaches the porous anodic oxide layer and promotes its partial sealing by hydration. This type of interactions has been described by Whelan *et al*. [8]. The hydration reaction improves the porous layer barrier properties, thus the impedance increases in that frequency region and the electrochemical response from the sol-gel barrier cannot be distinguished. In spite of this effect the total impedance of this "duplex" coating system reduced slightly with immersion time.

Excluding the anodized sampled, the coated sample treated with the additional oxide growth step (ACO) is the one that shows higher impedance values at all frequency range, reflecting not only

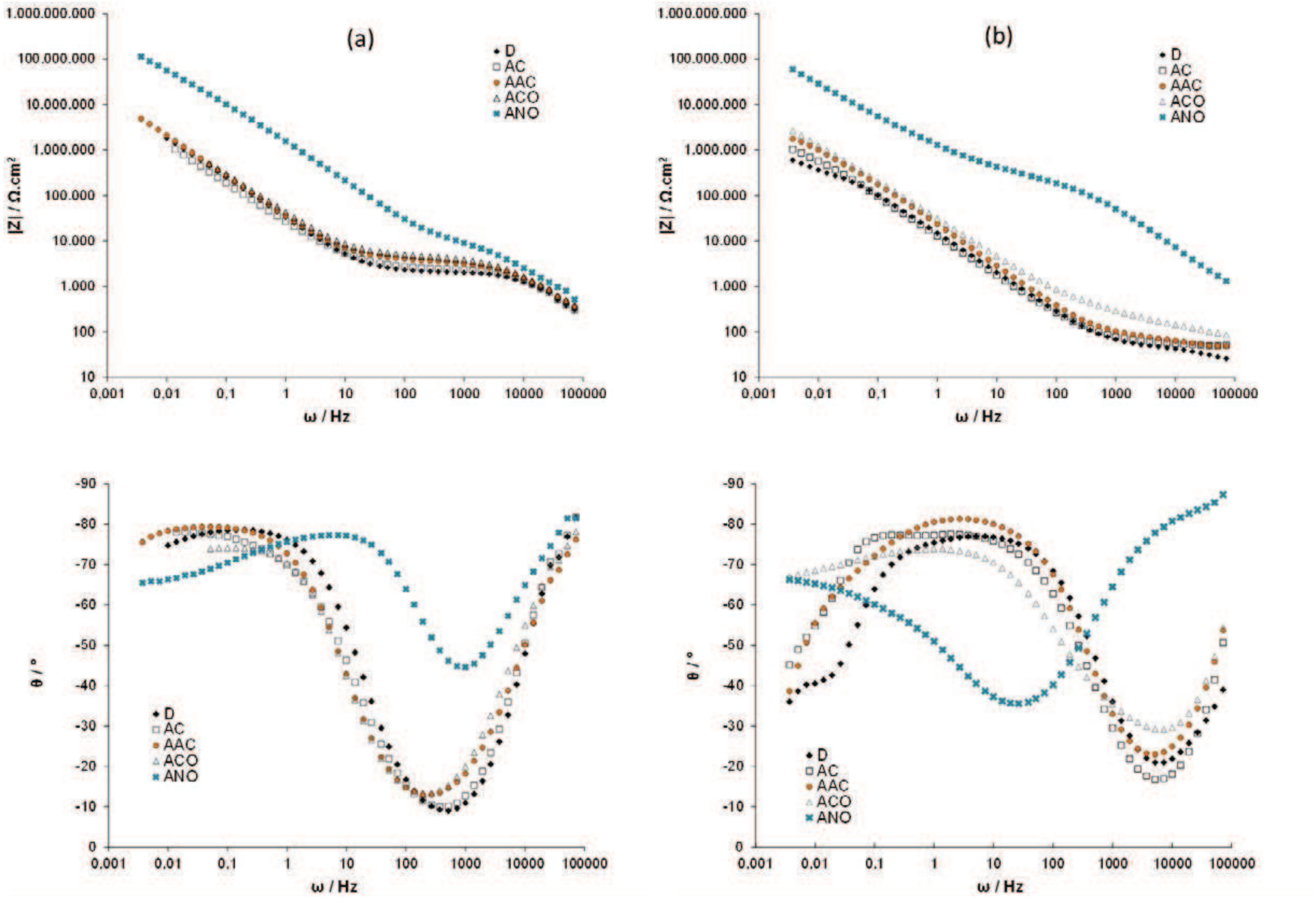

Fig. 3 - Bode plots obtained after (a) 1 h and (b) 28 days immersion in NaCl 0.5 M solution for the hybrid sol-gel coated aluminium alloy samples with different surface pre-treatments.

better corrosion resistance of the native oxide layer, but also better barrier properties of the sol-gel coating suggesting a synergic effect. Without additional oxide growth steps, the best corrosion behaviour was exhibited by the coated sample that was subjected to the alkaline plus acid cleaning (AAC) pre-treatment, what could be attributed to a higher reduced level of intermetallic compounds present on its surface, due to the very aggressive etching procedure applied (Fig. 1).The coated sample least corrosion resistant, based on EIS results, was the one only degreased (D). Therefore the EIS based ranking of corrosion resistance is in agreement with the visual aspect shown by the tested samples after 28 days of immersion.

3.2.2 Accelerated corrosion test

The corrosion performance of the different pre-treated hybrid sol-gel coated samples was also assessed by exposure in a wet chamber (40 °C; 82 % RH) after contact with HCl (38 %). Fig. 4 displays the visual aspect of the samples after 1000 h exposure. As can be seen all the coated samples, except the anodized one (ANO), developed pitting corrosion all over the coated surface. Pitting corrosion is more severe in the samples only solvent degreased (D) and less intense in the one subjected to the additional step of oxide growth (ACO). The sample subjected to the double etching (AAC) exhibited aggravated pitting localized around the scratches, similar to the only solvent degreased sample. The anodized sample (ANO) only shows corrosion inside the scribe. In general, these results are in good agreement with the EIS results and show the beneficial effect of intermediate oxide layer on the corrosion resistance of the sol-gel coatings under study.

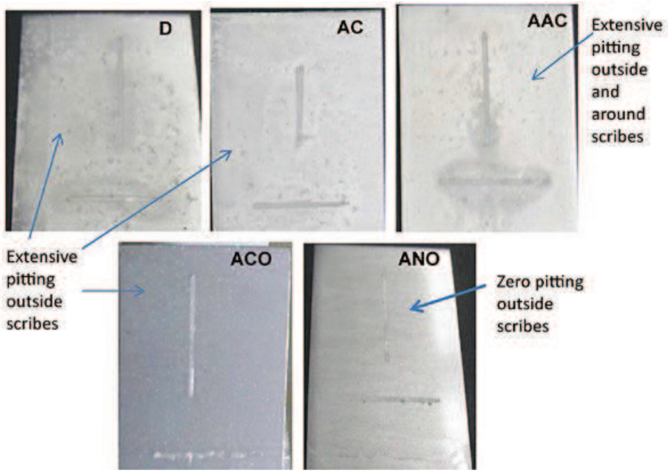

Fig. 4 - Visual aspect of sol-gel coated aluminium alloy samples with different pre-treatment after contact with HCl (38 %), followed by 1000 h exposure in the wet chamber.

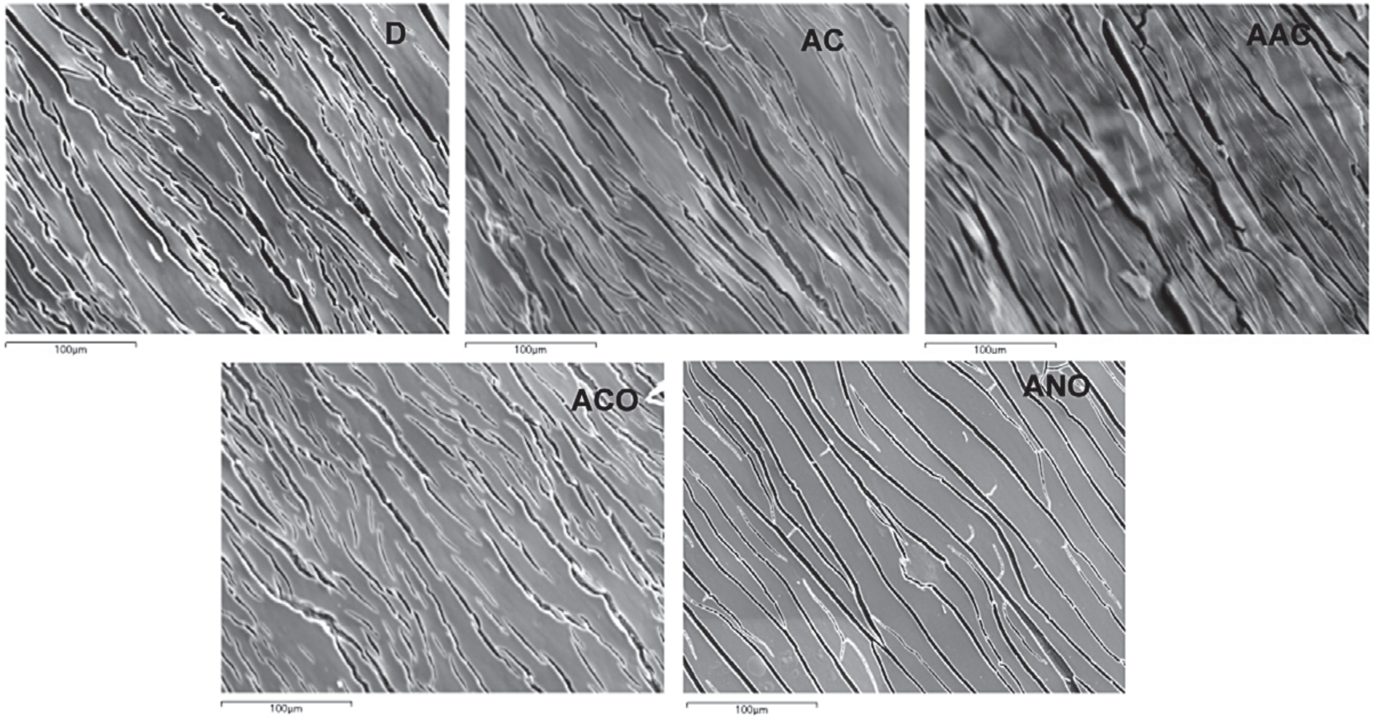

Fig. 5 - SEM micrographs of the bent surface of the different pre-treated hybrid sol-gel coated aluminium alloy samples after bending test.

3.2.3 Adhesion tests

Sol-gel coatings adhesive performance was evaluated in dry conditions by the cross cut test (ISO 2409 [14]) which yield a zero level of detachment for all samples. The bend tests (ISO 1519 [15]) were performed after exposure in the wet chamber, using a 5 mm diameter mandrel. SEM observation of the bent surfaces (Fig. 5) revealed intensive coating cracking after substrate deformation in all coated samples, although detachment of the coating was only visible in the alkaline plus acid cleaned (AAC) samples, probably due to their very smooth and less oxidized surface. Coating cracking, however, was less severe in the samples subjected to the additional oxide growing steps (ACO, ANO). These results reveal both the importance of the surface roughness and of the presence of an oxide layer for sol-gel coating adherence to the substrate which ultimately affects its corrosion performance. Also justify the partial inferior corrosion behaviour of the ACC treated samples in the accelerated corrosion test.

4. CONCLUSIONS

The results demonstrate that the metallic substrate pre-treatment influences the corrosion resistance of hybrid sol-gel coated EN AW-6063. The best anticorrosive performances were achieved by the coatings applied on the substrates treated by the combination of acid etching with oxide growth, showing the effect of both intermetallic compound particles removal and oxide layer thickening. Thickening this oxide leads to improved corrosion resistance and is beneficial to adhesive properties. SEM observations indicate less cracking after substrate deformation for these samples, while those subjected to the double alkaline plus acid etching with a smoother deoxidized surface exhibited the worst adhesive performance. In this case, the adhesive behaviour did not follow the corrosion behaviour, demonstrating the impact of substrate roughness on coatings adhesion.

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