SECM-10 Workshop
29 September -3 October 2019
Paris - Fontainebleau, France

SECM study of a chromium-free anticorrosion adhesion primer for aluminum 2024

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Hexavalent chromium, largely used for anticorrosion surface treatments of aluminum in aeronautics, will soon be completely banned due to its high toxicity (REACH regulation). Looking for an innovative solution, regarding both anticorrosion and adhesion properties, a chromium free replacement treatment directly inspired by the diazonium chemistry has been developed by the CEA (LICSEN). The evolution of the surface electrochemical properties was followed before and after grafting by means of scanning electrochemical microscopy (SECM). These studies showed that the native aluminum oxide layer is etched during the organic grafting step, which is performed in sulfuric acid. SECM also evidenced that the polymeric grafted film is porous enough to allow the reconstruction of this native aluminum oxide layer after the treatment. On the strength of these results, we decided to extend the thickness of the aluminum oxide layer by an anodization treatment, in the idea that Al_2O_3 could be formed through the organic layer without altering it. In that purpose, SECM was used to characterize the films and allow the determination of the best parameters for the organic coating (concentration, immersion time, diazonium function, rinsing, cleaning, additives…) and for the anodization process (duration, applied tension…). Thus, bi-functional coatings were obtained, giving very satisfying results both in terms of corrosion protection and adhesion with painting. This simple and low cost process has been patented(1). It validates standardized tests and could be swiftly industrializable.

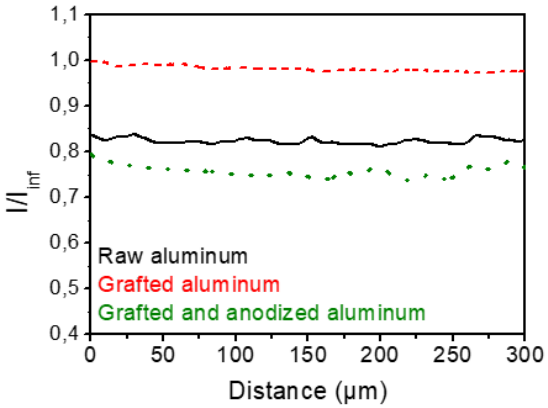

Figure 1 : SECM conductivity line scans obtained for raw aluminum (solid line), aluminum grafted with the 4-nitrobenzenediazonium (dashed line) and aluminum grafted with the 4-nitrobenzenediazonium and anodized (dotted line) ; I_{inf}=90 nA, R_g=50 µm, probe/substrate distance: 30 µm, Etip=0.5V, Esub=-0.8VvsAg/AgNO₃, in Fc/DMF (10mM) + TBAF (100mM), reference electrode : Ag/AgNO₃

(1) G.Charrier, A. Doublet, G.Deniau, C.Cornut, FR 1872018, deposited on Nov. 28th 2018