Influence of substrate pretreatments on the Trivalent Chromium Process (TCP) coating properties on aluminium alloys

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High strength aluminium alloys are widely used in the aerospace industry [1]. They are usually coated with a conversion layer, which enhances corrosion protection and allows for deposition of organic coatings [2]. The NAVAIR has patented a new conversion coating system based on trivalent chromium species (Cr^{III}) known as the Trivalent Chromium Process (TCP) [3]. The TCP contains typically hexafluorozirconate, chromium sulfate and pH-adjusters [4]. Although good corrosion properties can be achieved by the TCP coatings [5], there is still a lack of understanding of the deposition mechanisms and of the role of surface pretreatments in providing good deposition and corrosion performance of the TCP coatings.

The aim of this work was to test the various classic substrate pretreatments (degreasing and desmutting) and their influence, first, on the surface chemistry, and then, on the subsequent deposition of the TCP coating. Two different materials were tested, a pure aluminium (99.999 % at. purity) and an AA2024-T351 aluminium alloy. The surfaces after pretreatment and TCP deposition were analyzed by means of highly sensitive surface techniques, which are X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The TCP conversion coating was around 100 nm thick and it was mainly composed of zirconium di-oxide with a chromium oxide/hydroxide preferentially in the outer part of the coating (≤ 10 nm in depth). No chromate (Cr^{VI}) was detected by XPS.

As evidenced by XPS and ToF-SIMS analyses, the desmutting step significantly modifies the surface chemistry of AA2024-T351 aluminium alloy, by decreasing the native AI oxide layer thickness, by forming a thin aluminium fluoride layer for a fluoride-based desmutting bath, and by increasing and spreading copper on the AI alloy. Besides, an increase of surface roughness, which occurs during this step, seems to be detrimental for the deposition of the TCP layer. The best results in terms of coating homogeneity and its corrosion resistance (tested by Linear Sweep Voltammetry) were obtained for samples without desmutting pretreatments. The TCP coating deposited directly on a degreased aluminium alloy 2024-T351 -without desmutting step- covers completely the surface, and is thicker on some intermetallic particles like Al₂CuMg.

[1] J.R. Davis, Corrosion of aluminium and aluminium alloys, Ed. J.R. Davis, ASM international (1999).

[2] A.E. Hughes, B.R.W. Hinton, Surf. Interface Anal. 25 (1997) 223-234.

[3] C. Matzdorf, M. Kane, et J. Green, U.S. Patent 6 375 726 (2005).

[4] L. Li, G. P. Swain, A. Howell, D. Woodbury, G. M. Swain, J. Electrochem. Soc., 158(9) (2011) C274-C283.

[5] Y. Guo, G. S. Frankel, Surf. Coat. Technol., 206(19-20) (2012) 3895-3902.