

Study of Cr based and Cr-free Films on Al Surfaces:
A Complementary Approach

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Al alloys are often surface treated in order to improve mainly the corrosion resistance and to establish an adequate base layer for organic coatings. Chromium oxide and chromium phosphate layers have been applied for years providing excellent performance for a wide variety of applications. But as chromates are toxic and carcinogenic, alternatives are proposed such as zirconium-titanium oxide films, silane layers, self assembling molecular layers,.....

The objective of our study is to investigate the film formation mechanism on the aluminum substrate. It is clear from several studies that the corrosion and adhesion performance of the coated aluminum system is related with the pretreatment and the conversion cycle, used to form passive layers on the aluminum alloys prior to the organic painting. The approach used in these studies is to integrate all aspects; meaning aluminum alloy history, pretreatment cycle, composition of the conversion bath, and formation of the resulting thin film on the aluminum substrate. Therefore we combine in-situ electrochemical investigations based on e.g. open circuit potential measurements, ring – disc current measurements and impedance data with ex-situ surface analysis investigations.

In the work it was found that the surface characterization based on techniques such as XPS, AES, ToF-SIMS gives primordial information. However these methods are time consuming, require a high vacuum and the number of measurements that can be acquired are often limited. Therefore it will be shown how converted Al surfaces can be usefully characterized by means of their reflective properties. The major optical technique applied is Spectroscopic Ellipsometry (SE) which measures the polarization change of light due to interaction with the sample surface. It is called spectroscopic if the measurement is performed at various wavelengths. Accurate characterizations have been obtained for different film thickness even for chromium free conversion films of only a few nm thick. However, VIS-SE fails to give unambiguous chemical information due to the absence of characteristic features, e.g. absorption's, in the optical properties of the investigated materials. The same systems have been analyzed in the infrared. In this case it is found that the FTIR reflection-absorption technique (FTIR-RAS) enables the direct elucidation of the molecular composition of the various coatings without any prior sample preparation. An original approach has been followed by the use of the new infrared Spectroscopic Ellipsometry technique (IR-SE) which combines the advantages of VIS-SE to the characteristic chemical information revealed by FTIR-RAS.

1. J. De Laet, J. Vanhellefont, H. Terryn & J. Vereecken, *Appl. Phys. A*, **54** (1991) 72.
2. J. De Laet, H. Terryn, J. Vereecken & J. Vanhellefont, *Surf. Interf. Anal.*, **19** (1992) 445.
3. J. De Laet, J. Vanhellefont, H. Terryn & J. Vereecken, *Thin Solid Films*, **233** (1993) 58.
4. J. De Laet, H. Terryn & J. Vereecken, *Electrochimica Acta*, **41** (1996) 1155.
5. J. De Laet, H. Terryn & J. Vereecken, *Thin Solid Films*, **320** (1998) 241-252.
6. T. Schram, J. De Laet & H. Terryn, *Thin Solid Films*, **313-314** (1998) 727.
7. T. Schram, J. De Laet & H. Terryn, *J. of Electrochem. Soc.*, **145**, 8 (1998), 2733-2739.
8. T.Schram & H.Terryn, *J.Electrochem.Soc.*, **148**, 2 (2001), F12.
9. T.Schram, H.Terryn & A.Franquet, *Surf.Interf.Anal.*, **30** (2000), 507.