Benefits and difficulties of GDOES characterization of corroded surface: examples of Fe, Mn and Cl enrichment in corroded Mg

Alina MALTSEVA[1], Sviatlana LAMAKA[2], Nick BIRBILIS[3], Patrick CHAPON[4], Polina VOLOVITCH[1]

[1] Institut de Recherche de Chimie Paris (IRCP), France
[2] Magnesium Innovations Centre (MagIC), Helmholtz-Zentrum Geesthacht, Germany
[3] Monash University, Australia
[4] Horiba Scientific, France

Glow Discharge Optical Emission Spectroscopy (GDOES) permits depth profiling of solids due to a unique combination of a highly sensitive multi-element analysis with fast sputtering rate and high depth resolution with experimental simplicity. Its application to corroded surfaces is however still challenging because of not evident choice of analysis conditions able to ensure correct sputtering of porous corrosion products and not evident data interpretation because of significant plasma modification when sputtering the layers containing hydroxides. In this work, we report recent progress of GDOES application to analysis of Fe, Mn and Cl depth distribution in corroded Mg alloys. These elements were selected because the enhanced corrosion of Mg is often attributed to localized processes related to either Fe enrichment or the oxide film breakdown by Cl^-. Mn alloying decreases the detrimental impact of Fe [1] and recently [2] iron complexing agents were proposed as inhibitors of Mg corrosion. At the same time, the presence of organic molecules can limit the access of Cl^- to the interface. The verification of mechanistic hypotheses implies the development of analytical methods able to analyze depth distribution of these elements in corroded layers.

Corroded surfaces were obtained on pure Mg and MgMn alloys (up to 1.92 wt. % of Mn) with 50 -340 ppm of Fe at open circuit and under anodic polarization in Cl-containing and Cl-free solutions at different pH and with and w/o additives. Sputtering conditions were optimized and the effect of H in plasma on the analytical capacities and data interpretation was considered. The analysis of Mg alloys with different Fe and Mn composition was provided in Ar and Ar/H_2 plasma. Hydrogen in the plasma modifies intensities and background of some elements, making necessary to take into account the quantity of H in plasma for data interpretation. The direct interpretation of depth profile can be misleading, for instance a direct observation of Mn depth profiles obtained in Ar plasma suggests that the corroded layer is depleted in Mn while calculations taking into account H effect clearly show the Mn enrichment. The experiments in Ar/H_2 plasma demonstrated the enrichment by direct profile reading. Considering the distribution of Cl, it seems that H effect is less important; however, the GDOES demonstrates that some inhibitors suppress Cl enrichment in the oxidized layer and/or at the interface.

References:

[1] D.S. Gandel, N. Birbilis, M.A. Easton, M.A. Gibson, The Influence of Mn on the Corrosion of Al-Free Mg Alloys, 18th Int. Corros. Cong. 8 (2011) 1–9.

[2] S. V. Lamaka, B. Vaghefinazari, D. Mei, R.P. Petrauskas, D. Höche, M.L. Zheludkevich, Comprehensive screening of Mg corrosion inhibitors, Corros. Sci. 128 (2017) 224–240.