

Surface film evolution on pure magnesium during aqueous corrosion surveyed by *in-situ* Raman spectroscopy

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Reactivity of Mg alloys is strongly affected by the properties of the surface films. Thus, understanding of their formation mechanism in different environments is critical for development of intelligent anticorrosion strategy. The mechanism interpretation based on *ex-situ* analysis could be misleading due to the possible surface modification during sample preparation and analysis itself, therefore development of *in-situ* methodologies is necessary.

In this work we propose to use Raman spectroscopy for *in-situ* survey of the surface film evolution on pure Mg in aqueous environment and demonstrate the application of this methodology to investigation of solution composition effect: varied pH and presence of corrosion inhibitors.

In-situ Kinetics Raman Mapping (KRM) [1] was developed to survey the local film growth and breakdown under the thin layer of solution and extract kinetics laws from each location on μm -scale. KRM evidenced formation of $\text{Mg}(\text{OH})_2$ in all studied conditions; different kinetics trends of $\text{Mg}(\text{OH})_2$ growth was observed depending on solution composition and location on the surface (Fig.1). The bands at 3675 and 3710 cm^{-1} attributed to surface $-\text{OH}$ groups [2] and evidenced the high surface area (small grain size) of $\text{Mg}(\text{OH})_2$ were observed *in-situ* at $\text{pH} > 11$ and in presence of inhibitors. Detailed analysis of Raman and IR spectra revealed different types of inhibitors interaction with the surface film: physical and chemical adsorption, precipitation of coordination polymer.

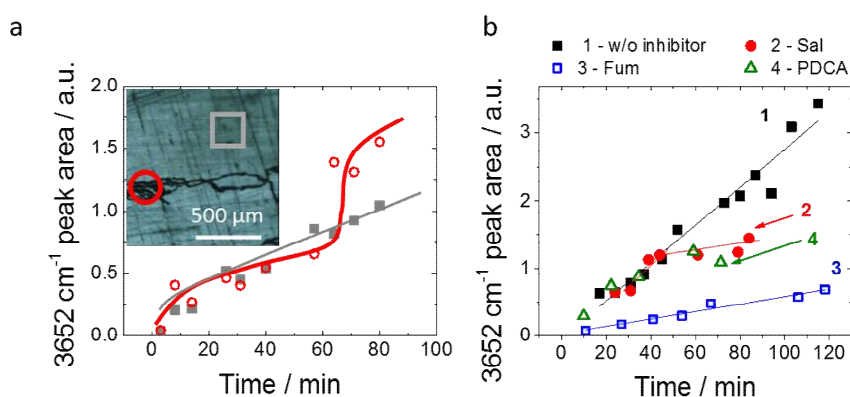


Figure 1. Growth kinetics of $\text{Mg}(\text{OH})_2$ on pure Mg in 0.1 NaCl solution: (a) pH 9 in areas with local attack and intact zone; (b) in presence of corrosion inhibitors (sodium salts of salicylic (Sal), 2,5-pyridinedicarboxylic (PDC) and fumaric (Fum) acids).

Références:

- [1] A. Maltseva, V. Shkirskiy, G. Lefèvre, P. Volovitch, accepted in Corros. Sci. (2019)
- [2] R. Zeitler, J.A. Greathouse, J.D. Gale, R.T. Cygan, J. Phys. Chem. 118 (2014) 7946