Controlling Localized Corrosion by Lateral Modification of Surfactant Inhibitors

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Corrosion and materials degradation is one of the most critical problems on our way to a more sustainable society. It is a serious phenomenon devastating materials reliability that causes irreversible damage and potential catastrophic failure of metallic structures, leading to large economic losses. Despite the plethora of reports on corrosion testing and inhibition at a macroscopic level, only few works aim to understand the basic processes driving materials degradation at the nanoscale. Alloy corrosion (dealloying) is often involved in localized and stress corrosion cracking, a major concern for the stability of metallic materials in general [1]. Localized dealloying in binary metallic alloys modified with self-assembled monolayers of organic molecules (SAMs) can be triggered by a local breakdown of the protective inhibitor film. The mechanisms behind localized dealloying initiation are far from being understood [2,3]. Corrosion initiation at the nanoscale can be addressed by controlling the spatial distribution and molecular organization of SAMs at the nano and micro length scales.

In this context, we introduce a multistep approach to create artificial molecular interfaces with well-controlled heterogeneous molecular organization at nano/meso length scales. Our study provides mechanistic insights into localized dealloying, unravelling the interplay and influence of both substrate and organic film properties on corrosion attack initiation and development. In particular, we used atomically flat single crystal Cu_3Au-100 surfaces with different surface morphology and modify them with alkanethiols of different chain length. For SAM modification we combined microcontact printing (µCP) and solution backfilling to build up films with well-controlled heterogeneity [4]. The inhibitor-modified surfaces were electrochemically dealloyed and characterized by atomic force microscopy (AFM) and focused ion beam scanning electron microscope (FIB-SEM) [5].

Our study reveals that the stability of the inhibitor molecules strongly depends on intermolecular forces between the inhibitor molecules and on the alloy surface morphology [5]. For large alloy surface terraces, dealloying preferentially initiates at the boundary region between areas where two different inhibitor molecules coexist. We show as well how atomic step density of the alloy surface strongly influences the morphology of the corrosion attack. Our work can be taken as a reference to study corrosion initiation processes at the nanoscale, to design inhibitor cocktails for corrosion prevention and to advance our understanding of nanomaterials stability.

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