In situ study of hydrogen-induced cavity/blister nucleation and growth at metal/oxide interface

Xie, D.[1], Li, M.[2] and Shan, Z.[1]

[1] Xi'an Jiaotong University, China, [2] Pittsburg University, China

The corrosion resistance of metals relies on a passivating surface layer of dense and adherent oxide. However, the integrity of such a protective oxide is compromised in the presence of excess hydrogen which can cause blistering and eventual spallation of the oxide film. So far it remains unclear as to how a nanoscale gas bubble manages to reach its critical size at the metal/oxide interface before the oxide layer can deform. Using in situ environmental transmission electron microscopy, we have discovered that once the aluminum metal/oxide interface is weakened by the segregating hydrogen, rampant surface-diffusion of Al atoms sets in to form numerous gas-accumulating cavities on the metal side driven by Wulff reconstruction. The morphology and growth of these metal-side cavities are found to be highly orientation sensitive. The surface oxide layer remains unyielding until the metal-side cavities grow to a critical size above which the accumulated gas pressure become strong enough to blister the oxide layer. Subsequently, we further conducted elevated-temperature investigation on the cavity evolution in hydrogenated metal. The results show that hydrogen exposure of just a few minutes can greatly sabotage the high temperature integrity of metal/oxide interface. Moreover, there exists a critical temperature of ~150 °C, above which the growth of cavities under the metal-oxide interface reverses to shrink, followed by the formation of a few giant cavities. Activation of a long-range diffusion pathway along the detached interface and the decomposition of hydrogen-vacancy complexes are critical factors affecting this behavior. Our findings have broad implications for coating performance in nuclear, petroleum, and transportation industries, and can help optimize the material design strategies to alleviate a broad range of hydrogen induced interface failures (Xie et al, Nature Materials, 2015 ; Li, Xie al, Nature Communications, 2017).

The authors acknowledge supports from the National Key Research and Development Program of China (No. 2017YFB0702001), the Natural Science Foundation of China (51701151), and the Natural Science Foundation of Shaanxi Province (2017JQ5110)