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Ab initio Study of the Mechanism for the Initiation of Localized Corrosion on Stainless Steel

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Changing the World's Energy Future

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SCIENTIFIC ACHIEVEMENT:

Stainless steels are widely used as primary piping material in PWR's because of their high corrosion resistance largely due to the formation of a passive film of metal oxides, such as chromium (e.g., Cr_2O_3). However, upon exposure to aggressive ions like chlorides (Cl^-), stainless steel becomes susceptible to localized corrosion due to the breakdown of the passive film. It is therefore essential to gain fundamental insights into the mechanism of the passive film breakdown (depassivation) to develop a tailored design to minimize localized corrosion. This project investigates the initial stages of the depassivation of the Cr passive film using density functional theory (DFT), a quantum based computational method. The mechanism of Cl^- induced depassivation has long been debated but two most popular models are the ion exchange (IE) model and the point defect (PD) model, illustrated in figure 1. Pit initiation in chloride containing solutions involves Cl^- adsorption on the surface, insertion by ion exchange with subsurface anion and migration of Cl^- through the oxide film (according to the ion exchange model) or Cl^- induced cation vacancy formation on the surface followed by vacancy migration to the metal/film interface (according to the point defect model).

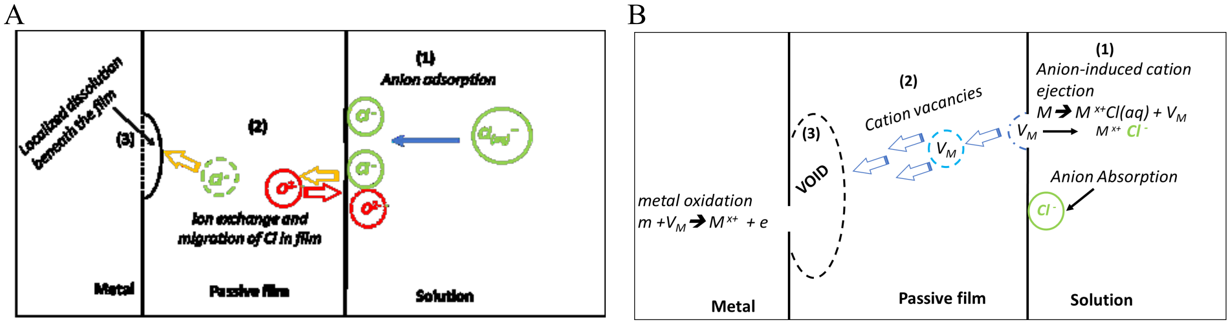

Fig.1. Schematic of the ion exchange (A) and the point defect models (B) describing chloride induced depassivation mechanism of metals and alloys in three stages, labeled (1)-(3). Both models start with anion adsorption but in the ion exchange model (A) the adsorption (1) is followed by Cl^- insertion by ion exchange (2) with sub-surface anion and migration through the film leading to localized dissolution at the metal/film interface (3). In the point defect model (B) the adsorption is followed by metal cation (M^{x+}), in a complex with Cl^-, ejection from the surface (1) and migration of cation vacancy (V_m) to the metal/film interface (2) leading to vacancy condensates forming a void at the metal/oxide interface (3).

Using density functional theory calculations and the high-performance computing (HPC) resources at INL we have compared the thermodynamic feasibility of certain critical steps of the two depassivation models. We found that the overall mechanism is concentration dependent interplay between the two models. At low chlorine (Cl) concentration/coverages substitution with weakly adsorbed surface species, H_2O/OH, is favorable but becomes unfavorable at higher Cl coverages. Cl insertion into the film is unfavorable at low coverages but becomes more favorable at higher coverages, supported by the IE model. The high Cl coverages and subsurface Cl, also enhance cation vacancy formation, which is supported by the PD model. This suggests that at high Cl coverages both Cl insertion, described by the IE model, and cation vacancy formation, described by the PD model, are thermodynamically favorable unlike for chloride enhanced depassivation of iron where only the PD model was found to be feasible. This implies that the initial stages of Cl induced breakdown of the chromium oxide passive film differs significantly from iron, a major component of stainless steels and can be described as an interplay of the two mechanisms which is concentration dependent in good agreement with experimental observations.

SIGNIFICANCE:

The outcome of this work will make a significant contribution to the knowledge about the role of Cl in the depassivation of the chromium oxide passive layer of stainless steel. This work is a part of an NEUP/NEAMS project which provides kinetic information at the atomistic level to understand and predict the localized corrosion on stainless steel. The overall project combines modeling and experiments to predict corrosion and embrittlement in dual-phase stainless steels within the MARMOT framework. The outcomes of the DFT and experimental work will be impactful in evaluating benefit the predictive capabilities for corrosion in MARMOT.

KEY PUBLICATIONS:

1. K. O. Sarfo, P.V. Murkute, Y. Zhang, O. B. Isgor, J. D. Tucker, L. Árnadóttir, First principles study of the initial stages of chloride enhanced depassivation of chromium oxide film (paper in preparation to be submitted to Corrosion Sc.)