First-principles modeling of passivation behaviors of stainless steels in corrosive environments

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Abstract Accurately determining the Flade potential (E_{Flade}) is of significant importance in the design of novel corrosion-resisting alloys. However, due to the complex nature of the E_{Flade} influenced by several factors including compositions of the alloys and corrosive solutions, there is currently a lack of truly predictive *ab initio* model. Here, we established the critical potential condition required for passivation in acidic solutions containing chloride ions (Cl^-) by developing an ab initio model that incorporates the potential drop from the metal electrode to the solution, considering tunneling of electrons at metal/film interface, breakdown of the film, and electrochemical adsorption reactions at film/solution interface. These parameters were derived from the work function of the alloy substrate and passivation film, the band gap of the passivation film, and the Gibbs free energy of adsorption on the passivation film, all of which can be obtainable from first-principles calculations. This theoretical model has been successfully validated for alloyed stainless steel, exhibiting a remarkable agreement with experimental results. Importantly, enabled by the model, we have identified several alloying elements (i.e., Ta, W, Os, and Ir) that can effectively lower the E_{Flade} of the stainless steel. This work constitutes an important step forward in modeling complex passivation behaviors from first-principles, providing a useful tool for the design of corrosion-resisting alloys.

Keywords Passivation, Modeling, First-principles calculations, Stainless steels