

Water Influence in Fe(100) corrosion process using MD simulation

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Abstract—Several simulations techniques has been used to understand chemical processes. Among them, molecular dynamics (MD) simulations have been demonstrated to be a powerful tool for studying several physical systems and new materials. In this work, the iron corrosion by water was studied by classical and *ab initio* MD simulations. MD simulation showed the formation of a water layer at about 2.5-3.0 Å, with hydrogen nearer of the iron surface than oxygen atoms. *Ab initio* simulations showed the breaking of chemical binding of water molecule and the absorption of hydrogen atom in the iron structure.

The natural corrosion process of metallic surfaces is of great interest for scientists and engineers. Experimental and theoretical studies have been used to proposal useful reaction mechanisms for decreasing the corrosion rate. Experimental and theoretical studies are contributing to increasing the understanding of interaction metals and chemicals related to corrosion processes. The iron corrosion process by water molecules was studied by computational methods: classical and *ab initio* molecular dynamics. DL_POLY 2.19 codes were used for classical MD and Car Parrinello Molecular Dynamics (CPMD) 3.13.2 codes were used for *ab initio* simulations. An orthorhombic box containing 565 water molecules over a ccc iron crystal with (100) surface exposed to water was used to study the adsorptions process with DL_POLY, using a simulation time of 100 ps at NVT ensemble with period condition. CPMD simulations ran into 20x20x20 box containing 108 Fe atoms in a ccc structure and one water molecule at 3 Å over the (100) iron surface. BHS-pseudopotential and xy periodic condition at 298 K were used.

Figure 1 shows the radial distribution function (RDF) for water oxygen and iron located at surface. The peak at 3 Å is an indication of strong interaction between the iron atoms at surface and water oxygen atoms. This interaction results on adsorption of water molecules at iron surface. The presence of multiple peaks in the Figure 1, indicates the formation of many water shells around the solid surface. Figure 1 shows the RDF curve for water hydrogen atoms and surface atoms of iron. The peak located at 2.8 Å shows that distance between hydrogen atoms and surface iron is lower than the distance between oxygen atoms and surface atoms of iron. This is a strong indication that the corrosion mechanism is initially related to hydrogen atom adsorption over iron surface. This conclusion was supported by *ab initio* results. Figure 2 represents the initial configuration used at CPMD simulations. CPMD's results indicated that the corrosion process runs by the following steps: break the molecules of water, adsorption of hydrogen atoms over iron surface and penetration of hydrogen atoms in the structure of iron. The penetration of hydrogen atoms into iron structure stresses the crystalline array, facilitating the corrosion process with the reduction of hydrogen and oxydation of iron atoms. These conclusions are supported by experimental results, where the adsorption and absorption of hydrogen atoms were studied by electrochemical analyses.

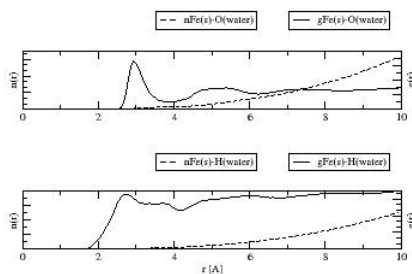


Figure 1: Radial distribution function of hydrogen and oxygen water molecule in water+Fe(100) system.

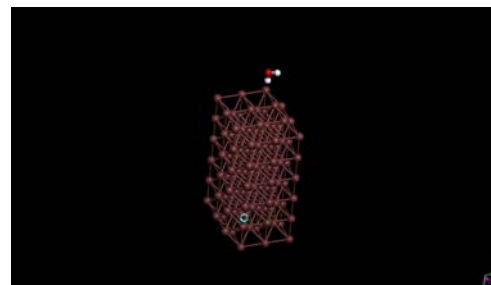


Figure 3: H-bond breaking and O-Fe bond near Fe(100) surface.