On the nature of the instability of the nascent magnesium oxide film: a first principles study

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Magnesium alloys have a high strength-to-mass ration that were it not for its corrosion problems would make it useful for light weight applications [1]. Magnesium is vulnerable to environmentally assisted cracking, run-away oxide formation, and other degradation processes [2]. This work serves as a starting point for understanding the atomic scale processes that ultimately lead to the oxide formation of magnesium.

In this work a detailed density functional theory analysis of oxygen binding to Mg(0001) and subsequent clustering is presented. The initial stages of oxygen adsorption to Mg(0001) are demonstrated to be subsurface. It is shown that magnesium mediates an attractive oxygen-oxygen interaction which ultimately leads to the formation of hexagonal clusters of O^* in the tetrahedral-1 site. The structure, work function, and binding properties of oxygen chemisorbed structures are compared with experiment to build a picture of the early stages of oxide formation over magnesium. A detailed comparison with previous surface science experiments of the O_2/Mg(0001) interface is presented and used for inference [3-6]. The early stage of oxide formation is describe as heterogeneous where the surface begins as (i) clean Mg(0001) and progresses to (ii) clean Mg(0001) with co-existing clusters of tetrahedral-1 O^* clusters to (iii) a triple phase of clean Mg(0001), clusters, and an MgO(111)-like structure.

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