Atomic Site-Specific Theory of H on γ U Surface

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Objective

This effort is a fundamental study of local chemical, electronic and physical behavior of metal and metal oxides as exposed to corrosive gases such as hydrogen and water vapor. The study benefits from state-of-art surface science experimental tools, such as scanning tunneling and atomic force microscopies (STM/AFM), photoelectron emission microscopy (PEEM), temperature programmed desorption (TPD) and modulated molecular beam mass spectrometry (MMBMS), to provide detailed knowledge of how, why and where a chemical reaction initiates and subsequently progresses with time, and theoretical/computational methods at the atomistic scale. The theoretical/computational component reported here consists of the first-principles calculation of the electronic structure of U surfaces exposed to H attack. The calculations were designed to shed light on the energetics of various configurations of H interstitial impurities on the surface or in the substrate of U bcc metal. Predictions as to the preference of H to occupy surface or substrate interstitial positions can be made on the basis of the configuration with the lowest ground-state total energy.

Description of the system

Uranium metal exhibits three allotropic phases with rising temperature: The orthorhombic, α , phase is stable up to 660 °C, with the tetragonal, β , phase becoming stable up to 760 °C. The bcc, or γ , phase studied here is stable above 760 °C. Uranium is known to be highly reactive with H, O, and H₂O. The preference of H to occupy surface or substrate interstitial positions can be determined by means of the energetics associated with the various competing configurations.

Details of the calculations

The energetics of free U surfaces, and surfaces containing H in selected interstitial positions were studied by means of state-of-the-art, highly precise electronic structure calculations based on a full-potential linear-muffin-tin-orbital (FPLMTO) code. In this approach, one treats the entire potential inside the Wigner-Seitz cell in a material, including non-spherical terms, rather than the spherical approximation to the potential that is often employed. Because of their proximity to the nucleus, the core states are determined fully relativistically, through a solution of the Dirac equation, while band states are treated semi-relativistically but with spin-orbit coupling taken into account in a self-consistent way. The wave function is expanded in energy and linear terms are kept. The calculation consists of an energy minimizing process in which the coefficients

of expansion are determined, leading to the wave function for the system and related quantities, such as the total energy.

The surface of U was simulated by means of a five-layer slab that repeats periodically along the z-direction. It was checked that the electronic structure at the center of the slab reproduces accurately that of bulk U in the bcc structure. Correspondingly, the electronic structure at the edge of the slab is taken to model that of the surface.

The energetics and structural stability of hydrogen at selected interstitial positions on the surface as well as in subsurface regions of pure U in the BCC structure were studied. Energetics information allows one to determine the propensity of hydrogen to either stay at the surface or penetrate deeper into the substrate. Thus, a lower energy of the system with hydrogen at the surface implies a more stable configuration than with hydrogen in the substrate and leads to the conclusion that hydrogen will not penetrate into uranium. It should also be kept in mind that in these initial calculations the effects of oxygen on the uranium surface are not considered, and this presence may indeed change the energetics substantially in both quantitative and qualitative ways. We also neglected relaxation effects, i.e., the possible displacement of U atoms from their equilibrium configurations that can arise because of the surface geometry as well as the presence of impurities such as H.

Results

Results of the electronic structure calculations of U and hydrogenated U surfaces are shown in Fig. 1. The figure depicts the f-electron density of states (DOS), i.e., the number of electronic states of f character per unit energy as a function of energy. The quantities shown here are associated with a U Wigner Seitz cell and are commonly referred to as local DOS (LDOS). Such densities of states figure prominently in the calculation of the total energy of the ground state of the system in various configurations. The upper panel shows a comparison of the DOS for bulk U (dark line) with that of U surface (light curve). We note that the surface DOS is considerably narrower than that of the bulk, as is indeed expected because of the reduction in coordination (number of near neighbors) associated with the surface geometry. The lower panel compares the DOS of a free U surface (light line) with the LDOS of a U atom next to a H interstitial (dark line). Note that the light curve in the lower part is identical with the dark curve in the upper panel. The differences between the two LDOS's in the lower panel are caused by the presence of H and similar differences can be calculated for other configurations, such as when the H occupies substrate interstitial positions (not shown). Such differences lead to corresponding differences in the ground state energy of the system in various configurations.

In the present case, hydrogen is energetically favored to occupy an interstitial site on the surface layer by about 0.15 eV, compared to subsurface layers. As mentioned above, more realistic calculations should be carried out which allow the study of the effects produced by the presence of other impurities, e.g., O, as well as the effects of lattice relaxation. During the past year, the codes for calculating the electronic

structure were extended to allow the study of lattice relaxation. Possible future calculations will take account of such effects.

Fig. 1. DOS's for (001) surfaces of bcc U metal (upper panel) and hydrogenated U (lower panel) as discussed in the text.

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