INVESTIGATE OF OXYGEN ADSORBED ON THE IRON (1 0 0) SURFACE FROM FIRST PRINCIPLES CALCULATIONS

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ABSTRACT

Electronic and structural properties of atomic oxygen adsorbed on the iron (100) surface are examined using density functional theory (DFT) calculations. The atomic oxygen is adsorbed at top, bridge and hollow sites. The properties of oxygen adsorbed on the iron (100) surface are investigated at the three adsorption sites. The calculated results are compared with the experimental and other theoretical results. The oxygen atom adsorbed on the hollow site is found to be the most stable, which is in agreement with experiment.

INTRODUCTION

Iron, a technological material of immense importance, has been studied both theoretically and experimentally for many years. The surface properties such as surface energy are important in determining electronic properties of a metallic surface and affect properties like adsorption, formation of grain boundaries, the form of crystallites and surface segregation. Pure iron may crystallize in several different structures. The primary structure is the α-phase, which adopts the bcc crystal structure. Experimentally, low-energy electron diffraction (LEED) has been used to examine the iron (100) surface [1, 2]. As regards theory, quantum mechanical methods such as DFT can be used to understand the electronic properties of surfaces.

Investigations of clean and adsorbate covered iron surfaces are of fundamental interest to improve the understanding of the initial interaction between Fe and gas. During the last decade, several theoretical and experimental studies of the oxygen adsorption on iron surface have been performed [3, 4, 5, 6]. K.O. Legg *et al.* [2] used LEED to show that O atom adsorbs 0.53±0.06 Å above the surface in a hollow site, and the spacing between the first and second iron layers is increased by about 7.5% to 1.54±0.06 Å at room temperature. In a theoretical investigation, Błoński *et al.* [4] concluded that the oxygen atoms lie in the hollow sites, 0.45 Å, using the spin-polarized generalized gradient approximation. In the present work, the adsorption of O in the top, bridge and hollow sites of Fe (100) in a p (1x1) arrangement, and the related energetics, surface geometry and charge density distribution of the system are examined. Our calculated results are compared to the available experimental and theoretical results.

METHODOLOGY

Density functional theory (DFT) plane wave pseudopotential calculations were performed using the Vienna Ab-intio Simulation Package (VASP) [7, 8]. The exchange-correlation energy is described using the Perdew and Wang (PW91) [9] form of the spin-polarized generalized gradient approximation (GGA). Especially the generalized gradient approximation (GGA), has been shown to yields ground state properties of iron in good agreement with experimental observations [10, 11]. The plane wave cutoff energy is 270 eV. Core electrons are replaced by ultrasoft pseudopotentials [12].

In the calculation, the k-space integrations were performed applying a 9x9x9 grid for the bulk crystal calculations, whereas a 9x9x1 mesh is used for the surface properties calculations. The quality is improved by using the first order Methfessel-Paxton [13] method with a smearing width of 0.2eV. The isolated O atom is modeled in a 15x15x15 Å cell and the energy cutoff is the same as that used for Fe. The size of the vacuum between slabs was set to 11.4 Å and the Fe (100) is modeled using an 5-layer [1x1] slab Figure 1.

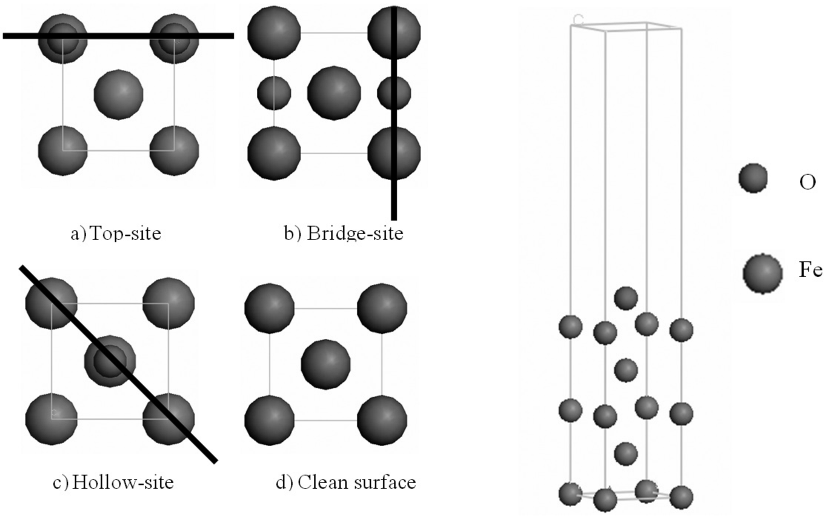

Figure 1: The model of oxygen atom adsorbed on the Fe (100) surface. Top view of a) top, b) bridge and c) hollow adsorption sites. The solid lines indicate directions of the charge density slices presented in Figure 2

The surface energy is the work required to form a unit area of surface, and is the solid analog of the surface tension of a liquid [14]. In the present work, it can be simply calculated as the difference

$$\gamma = (E_{slab} - E_{bulk}) / 2 \tag{1}$$

Where E_{slab} is the total energy of the slab, E_{bulk} is the total energy of the bulk crystal and n is the number of bcc unit cells in the slab.

The adsorption energy E_{ad} per O atom of the surface is determined as

$$E_{ad} = (E_{slab+O} - NE_O - E_{slab}) / N \tag{2}$$

Where E_{slab+O} is the total energy of the relaxed O/Fe (100) system, E_{slab} is the total energy of the relaxed clean Fe (100) slab, E_O is the total energy of an isolated O atom, and N is the number of oxygen atoms per unit cell.

RESULTS AND DISCUSSION

As of a test of the reliability of the calculations, the total energy and the lattice parameter *a* of bulk bcc iron were calculated. Using the converged parameters, the bulk properties were calculated using GGA functions. The computational results are summarized in Table 1, where even a comparison with experimental results is also presented. From Table 1 it can be seen that the lattice parameter a is 2.884Å, which is 0.06% higher than the experimental values [15].

Table 1: Structure and properties of bulk bcc Fe

	Lattice constant a(Å)	**Cohesive energy (ev)**	**Magnetic moment (μ_B)**
This work	2.884	4.893	2.52
Expt. [15]	2.866	4.28	2.22

Extending the calculations to the surface, in the present calculations, surface relaxations are performed. The Fe (100) surface is cleaved from a crystal structure of bcc Fe, corresponding to the (100) Miller plane and modeled in 5 layers, which is evaluated by the convergence test, shown in Figure 1. A vacuum spacing of 11.4 Å was inserted in the z-direction between surface slabs. This vacuum size was seen to be sufficient to avoid the nonphysical interactions between slabs in the setup. A lattice constant of 2.884 Å was used in the calculations (the bulk cell lattice constant obtained from GGA). The oxygen atoms lie 1Å above the Fe (100) surface. In our calculation, the adsorption energy of oxygen atom is evaluated in the three different sites, top, bridge and hollow, as shown in the Table 2. In agreement with experiment [2], the hollow site on the Fe (100) surface is found to be the most stable. This also agrees with the ab- initio calculation [4].

Table 2: Adsorption energy of O atom adsorbed on the Fe (100) surface in the top, bridge and hollow sites

	Top site	**Bridge site**	**Hollow site**
Adsorption energy (eV)	-5.585	-6.632	-7.577

For 1 ML coverage, a summary of the calculated adsorption site geometries is presented in Table 3. In the hollow site, the oxygen atom lies 0.413 Å above the first iron layer, which is in agreement with the experimental results 0.536±0.06 Å, while 2.081 Å from its neighbours in the first iron layer and 2.04 Å above the second iron layer. The distances between the oxygen atom and its five nearest iron atom are almost the same, closely corresponding to the value of 2.15 Å in the bulk FeO, which indicate the formation of oxide-like bonds upon sufficient exposure of Fe (100) to oxygen [16]. The height of O atom above the Fe (100) surface decreases for the top, bridge and hollow sites, respectively. Compared with the clean Fe surface, the oxygen atom induces an expansion of the distance between the first and second layers.

Table 3: Calculated geometry values of clean Fe (100) surface and O/Fe (100) obtained for the Fe (100) surface

Site	**D_0Å**	**D_{12}Å**	**D_{23}Å**	**Reference**
Clean surface	-	1.218	1.479	Present work
bridge	1.053	1.609	1.420	Present work
top	1.589	1.361	1.443	Present work
hollow	0.413	1.629	1.452	Present work
	0.53	1.54	1.43	Experiment [2]

* D_0 is the height of O atom above the first layer, D_{12} is the distance of the first and second layers, and D_{23} is the distance between the second and the third layers

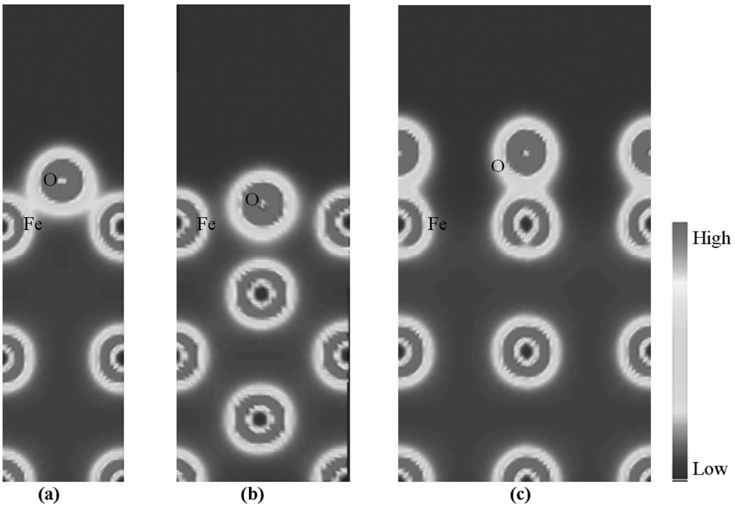

Figure 2: Charge density plots of oxygen atom adsorbed on the Fe (100) surface in a) bridge b) hollow and c) top of adsorption site

The total charge density plots for oxygen atom adsorbed in the three different sites are shown in Figure 2, the slices directions are indicated in Figure 1. In the Figure 2 (a), the total charge density for the bridge site indicates that O atom is directly bonded to its two nearest neighbour Fe atoms, and charge accumulation between these atoms. The total charge density of the hollow site (Figure 2 (b)) shows an accumulation of charge between the oxygen atom and the five nearest neighbour Fe atoms in the first and second layers. In the Figure 2 (c), an accumulation of the charge can be seen between the O atom and the nearest Fe in the first layer, which may make the first iron layer move to the second iron layer.

The adsorption of oxygen on Fe surface and energy calculations associated with the same have significance in modeling the slag-metal reactions using the above calculation methods. Oxygen is a surface active element and in oxidic melts, there is likely to be an oxygen accumulation on Fe surface. The situation is akin to the metal-gas interface with respect to the surface of metallic Fe. The present work is expected to be the first step towards an understanding of the slag-metal interfaces and the energies involved by means of *ab initio* calculations.

CONCLUSIONS

In conclusions, the present calculations indicate that the most likely adsorption site of O atom on Fe (100) surface is a hollow site, which is in agreement with experiment. The bridge and top site are less favoured, with the top site being least stable. The distance of the O atom on the iron (100) surface is the highest in the top site, and decreased in the bridge and hollow sites. The total charge density plots correlate with the geometry of the O and Fe atoms in the three different sites, showing O bonds to the closest Fe atoms.

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REFERENCES

Ueda, K. & Shimizu, R. (1972). *LEED-Work Function Studies on Fe (100)*. J. APPL. PHYS. 11, 916-917. [1]

Legg, K. O., Jona, F. P., Jepsen, D. W. & Marcus, P. M. (1975). J. Phys. C: Solid State Phys. 8, L492. [2]

Busch, M., Gruyters, M. & Winter, H. (2006). *Spin Polarization and Structure of Molecular Oxygen Adsorbed on Fe (110)*. Surf. Sci. 600, 4598. [3]

Błoński, P., Kiejna, A. & Hafner, J. (2005). *Theoretical Study of Oxygen Adsorption at the Fe (110) and (100) Surfaces*. Surf. Sci. 590, 88. [4]

Weissenrieder, J., Göthelid, M., Månsson, M., Von Schenck, H., Tjernberg, O. & Karlsson, U. O. (2003). *Oxygen Structures on Fe (110)*. Surf. Sci. 527, 163. [5]

Schröder, E., Fasel, R. & Kiejna, A. (2004). *O Adsorption and Incipient Oxidation of the Mg(0001) Surface*. Phys. Rev. B, 69, 115431. [6]

Kresse, G. & Hafner, J. (1993). *Ab Initio Molecular Dynamics for Liquid Metals*. Phys. Rev. B, 47, 558. [7]

Kresse, G. & Hafner, J. (1994). *Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal–Amorphous-Semiconductor Transition in Germanium*. Phys. Rev. B, 49, 14251. [8]

Perdes, J. P., Chevary, J. A., Vosko, S. H., Jackson, K. A., Pederson, M. R., Singh, D. J. & Fiolhais, C. (1992). *Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation*. Phys. Rev. B, 46, 6671. [9]

Bagno, P., Jepsen, O. & Gunnarsson, O. (1989). *Ground-state Properties of Third-row Elements with Nonlocal Density Functionals*. Phys. Rev. B, 40, 1997. [10]

Moroni, E. G., Kresse, G., Hafner, J. & Furthmüller, J. (1997). *Ultrasoft Pseudopotentials Applied to Magnetic Fe, Co, and Ni: From Atoms to Solids*. Phys. Rev. B, 56, 15629. [11]

Vanderbilt, D. (1990). *Soft Self-consistent Pseudopotentials in a Generalized Eigenvalue Formalism*. Phys. Rev. B, 41, 7892. [12]

Methfessel, M. & Paxton, A. T. (1989). *High-precision Sampling for Brillouin-Zone Integration in Metals*. Phys. Rev. B, 40, 3616. [13]

Fiorentini, V. & Methfessel, M. (1996). *Extracting Convergent Surface Energies from Slab Calculations*. J. Phys: Condens. Matter 8, 6525-6529. [14]

Kittel, Ch. (1986). *Introduction to Solid State Physics*. 6th edition (Joha Wiley, New York), PP. 23, 55 and 57. [15]

Brucker, C. F. & Rhodin, T. N. (1976). *Oxygen Chemisorption and Reaction on Fe (100) Using Photoemission and Low-Energy Electron Diffraction*. Surf. Sci. 57. 523. [16]