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Adhesion Energy of the Fe(BCC)/Magnetite Interface within the DFT approach

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Abstract

In Industrial applications, the mechanical stability of oxides formed on metallic alloys is a key concern in the determination of component susceptibility to different corrosion mechanisms. In this context, the energy of adhesion is an important parameter. Density functional Theory (DFT) and other atomistic methods are fundamental tools in the determination of this quantity for Metal/Oxide interfaces. In this paper Fe(BCC) /Magnetite interface is assessed within the DFT approach. An Universal Binding Energy Relation (UBER) model is used to calculate the interfacial separation at equilibrium and the adhesion energy.

Keywords: Work of Adhesion; Work of Separation; Interface; UBER; DFT; Iron; Magnetite.

1. Introduction

The integrity of the oxide scales formed on metallic alloys used for industrial applications is of key importance when assessing corrosion resistance of the alloy. Mechanical voids on protective scales may initiate localized corrosion mechanisms. In addition, particles originated in oxide spallation may derive in the erosion of a remote component of the system. Deposition of these particles as strange material or contamination agent is also a possible issue.

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The study of mechanical integrity of oxide scales has become a major concern during the last decades. A classification of fracture modes has been classified by Schütze (Schütze, 2005; Schütze et al., 2009) depending on the stresses affecting the oxide scale and crack orientation in relation with metal/oxide interface. The authors also review failure criteria for each case. Spallation failure is cited as an example. This failure mode can be found in systems with a weak interface in relation to the oxide, and under compressive stress. Crack nucleation and growth can be originated in deformations, when a critical deformation $\varepsilon_c$ is reached. This parameter can be calculated as a function of the oxide elastic constants $E_{Ox}$, $\nu_{Ox}$, the oxide scale thickness $\delta$ and the interface fracture energy $\gamma$,

$$\frac{1}{\varepsilon_c} = \left[ \frac{1}{2\gamma} \frac{\partial E_{Ox}}{\partial (1-\nu_{Ox})} \right]^{1/2}$$  \hspace{1cm} (1)

Another possible case is the breackage of the oxide scale due to a temperature diference $\Delta T$ (cooling) as a function of the difference in the thermal expansion coefficient $\Delta \alpha$,

$$\frac{1}{\varepsilon_c} = \frac{\gamma}{E_{Ox}(\Delta \alpha)^2(1-\nu_{Ox})}$$  \hspace{1cm} (2)

From these examples, it is evident that interfacial fracture energy must be determined precisely if these models are pretended to attain predictive power. Experimental methods for determining this quantity exist, but are scarce and difficult. Hence, the problem has been assessed computationally. In particular, density functional theory (DFT) has been widely applied to interface decohesion (Eremeev et al., 2009; Jiang et al., 2010; Matsunaka and Shibutani, 2008; Udagawa et al., 2010).

In this context, the Fe / Fe$_3$O$_4$ system is of key technologic importance. Magnetite (Fe$_3$O$_4$) is a ferrimagnetic oxide with inverse spinel structure. Within the oxide scale produced when iron alloys are corroded by an oxidizing environment, the inner layer is magnetite or an oxide of similar structure and composition (Davenport et al., 2000; Toney et al., 1997; Yi, 2004). Hence, the knowledge of the surface fracture energy on the Fe / Fe$_3$O$_4$ system is essential.

2. Method


2.1. Bulk Calculations

Magnetite has an inverse spinel ($Fd\bar{3}m$) structure. The internal degrees of freedom are fully relaxed to obtain the ground state unit cell as shown in Figure 1. In this structure, oxygen can be found forming an FCC lattice, while iron is occupying the tetrahedral and octahedral sites. These iron sublattices are antiferromagnetically coupled (Rowan et al., 2009; Zhang and Satpathy, 1991). Along the (001) direction, atomic layers alternate their composition between Fe and FeO$_2$. Total energy is calculated as a function of the cell volume and fitted to a Birch-Murnaghan equation of state to obtain the lattice parameter (Birch, 1938). Lattice parameters are found to be $a_{Fe} = 2.842$ Å for ferromagnetic BCC iron and $a_{Fe_{3}O_{4}} = 8.395$ Å for magnetite. The MP was taken 7x7x7 for bulk magnetite and 15x15x15 for BCC iron to get a convergence of 0.1 meV.
2.2. Interface Calculations.

Davenport and collaborators (Davenport et al., 2000) obtained the orientation relationship between the BCC iron substrate and magnetite grown on it. They found that one of the most common orientations is \( \text{Fe}[001] \parallel \text{Ox}[001] \parallel \text{Fe}[100] \parallel \text{Ox}[110] \). They observe that this relationship is related to the fact that in the [110] direction, the interatomic distances on BCC iron are almost equal to the distances in the [100] of the oxide. However, interfacial separation distance cannot be determined experimentally.

Figure 2 shows the model supercell used for interface calculations. Two equivalent interfaces are included to minimize the supercell size. Oxide and metal slabs are located at each side of the interface with the orientations described above. In the central region, 11 atomic layers form the oxide slab, while 7 atomic layers are disposed as the BCC iron slab. As explained earlier, (001) planes alternate their composition. Hence, two terminations are possible for the oxide. The amount of 11 atomic layers for the oxide is the minimum required to represent one unit cell and assure that both terminations have the same composition. In order to accomplish periodic boundary conditions and coherence between the oxide and metal slabs, a compression of 4.3% is introduced in the oxide along the [100] and [010] directions. The total energy of the system is calculated as a function of the interfacial separation \( d \).

The interface formed by the oxide with FeO\(_2\) termination was studied in a previous work (Forti et al., 2012). In this work the interface with Fe terminated oxide is treated, were two piling possibilities can be taken into account. In the hollow piling (Fig 2(b)), iron atoms in the oxide surface are placed at a distance \( d \) above the octahedral sites of the metal surface. In the other hand, the top piling (Fig 2(c)) is obtained by placing the iron atoms on the oxide surface over the iron atom on the metal surface. It can be observed that both pilings are differentiated by a translation of the oxide slab by a quarter of the lattice parameter along the [100] direction, as visualized in the Figure 2.

The Energy of Adhesion \( E_{ad} \) is defined as the energy needed to separate the surfaces that conform the interface.

\[
E_{ad} = \frac{1}{2A} \left[ E(d) - (E_{Ox}^{slab} + E_{Me}^{slab}) \right]
\]  

(3)

where A is the surface area, \( E(d) \) is the supercell total energy when the interfacial separation is \( d \), and \( E_{Ox,Me}^{slab} \) are the isolated slab energies for the oxide and the metal, respectively. The \( \frac{1}{2} \) factor is originated in the fact that two interfaces are present in the supercell. In these interface calculations, as well as for the isolated surfaces, Brillouin zone integrations are performed in a MP grid of \( 7 \times 7 \times 1 \).
Magnetic coupling between contiguous slabs must be taken into account, because BCC iron and magnetite are materials of strong magnetic nature. The coupling possibilities are schemed in figure 3. Depending on the magnetic moment of the surface layers on each material, it is possible to have ferromagnetic coupling (FM), antiferromagnetic of type I (AFMI) or antiferromagnetic of type II. In FM coupling, the magnetic moment at each side of the interface is positive. In the AFMI coupling, the magnetic moment of the surface atomic layer is oriented outward from the surface, while in the AMFI coupling, the magnetic moment is oriented inward from the surface. Within the model of supercell chosen, it is not possible to distinguish between the AFMI and AMFI configurations. Hence, an extra calculation was performed with only one interface at the equilibrium interfacial distance measured for the chosen model supercell. An 8 Å is introduced in order to avoid interaction of the free surfaces with their mirror images. Energy differences between the AFM, AFMI and AMFI configurations were found to be negligible in comparison to the adhesion energies calculated with the same model. Hence, it is thought that the supercell model adopted here (figure 2) will not incur in important errors regarding this issue. It must be taken into account that even when the supercell with one interface only can be built with the same amount of atoms present in the model with two interfaces, in the first case the supercell is bigger than in the last one, due to the presence of a wider vacuum. Then, given that VASP expands wave functions in plane waves, the presence of this vacuum requires a greater calculation effort.

3. Results and Discussion

Results for adhesion energy as a function of interface separation are shown in figure 4 for all the studied terminations and both pilings for the Fe termination of the oxide. In order to obtain the interfacial energy, results are fitted to a Universal binding energy relation (UBER) (Rose et al., 1981) which is expressed in the following mathematical expression:

\[ E_{ad} = -\gamma \left( 1 + \frac{d - d_o}{l} \right) \exp \left( -\frac{d - d_o}{l} \right) \]  

(4)

where \( d_o \) is the equilibrium interfacial distance, \( \gamma \) is the interfacial energy, and \( l \) is a scale parameter. For a generic interfacial energy \( d \) atomic positions are fixed. Results for \( \gamma \) and \( d_o \) on the different systems are detailed on Table 1.

The configuration in which the oxide surface has composition Fe and the piling of the oxide and metal is of the hollow type results to be that of greater cohesion. It is observed that the relative position of the atomic layers imprints a greater change than the change in composition of the surface layers.
Fracture energies for Fe₃O₄ in different orientations and terminations as obtained by Liao and Carter (Liao and Carter, 2010) from DFT calculations are greater to 3 J m⁻². This fact indicates that the oxide is more resistant than the Fe (CC) / Fe₃O₄ interface. According to Evans (Evans, 1988) a compression in the oxide/metal interface with these relation of fracture energies between the oxide and the interface, oxide scale blistering may occur, where the interfacial crack would grow until the oxide spalls, leaving an area of the metal unprotected.

A few methods have been developed for experimental determination of the interfacial energy on metal/oxide systems. Some of them can be mentioned here: the inverse blistering test which is used to determine the adhesion of metallic films on oxide substrates (Mougin et al., 2002) the micro-tensile test which is preformed inside a scanning electron microscope (Toscan et al., 2004), generally used to measure adhesion of oxide thin films on metallic substrates, and the macro-tensile stress test aided by optic microscopy used to measure adhesion of thick oxide films on metallic substrates (Nilsonthi et al., 2013).

For the micro and macro tensile test, the oxide scale is grown on a metallic sample substrate at high temperature. After cooling of the sample, the oxide is induced into a compressive state. When the tensile test evolves, the compression is relaxed along the elongation axis to proceed into a traction state. On the contrary, in the transversal direction, compression is intensified when the sample is elongated, due to the volume conservation of the metal in the plastic regime. This effect causes the oxide scale delamination. Both effects are added to the elastic energy accumulated in an oxide spall generated to release stress. The knowledge of the released surface area from optical or electronic microscopy allows to compute the interfacial energy. The details of the mathematical model for these calculations are presented in references [galerie2004 and toscan 2004]. This kind of test was performed in the determination of the only value available, as far as we know, for the interface energy in a system consisting of low carbon steel and its oxide (Nilsonthi et al., 2013). The authors report a value of 2 J m⁻², which is really close to the values reported in this work.

Table 1. Results.

<table>
<thead>
<tr>
<th>System</th>
<th>γ (J m⁻²)</th>
<th>dₗ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(BCC) / Fe₃O₄</td>
<td>1.93</td>
<td>1.8</td>
</tr>
<tr>
<td>Fe₃O₄ (=Fe),hollows</td>
<td>1.04</td>
<td>2.2</td>
</tr>
<tr>
<td>Fe₃O₄ (=Fe),tops</td>
<td>1.41</td>
<td>1.9</td>
</tr>
<tr>
<td>Fe₃O₄(=FeO₂)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4. Conclusions

Surface magnetite stability has been studied within the density functional theory and using a UBER model. Relative orientations between metal and oxide structures were obtained from experimental observations available in the literature. It was found that the most stable interface is found for an Fe termination of the oxide and for the piling with the metal on the hollow sites. It was also possible to find the interfacial fracture energy. The result is in good agreement with scarce experimental results available. Hence, it would be possible to use the method to build a comparative base between different metal/oxide interfaces.

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References