Wear 274–275 (2012) 281–285

Contents lists available at SciVerse ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

On the film thickness dependence of shear strengths in sliding, boundary-layer friction

Michael Garvey[a], Michael Weinert[b], Wilfred T. Tysoe[a,*]

[a] Department of Chemistry and Biochemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, 3210 N Cramer Street, Milwaukee, WI 53211, USA
[b] Department of Physics and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, 2200 E. Kenwood Blvd., Milwaukee, WI 53211, USA

ARTICLE INFO

Article history:
Received 12 May 2011
Received in revised form
14 September 2011
Accepted 21 September 2011
Available online 29 September 2011

Keywords:
Density functional theory
Shear strength
Pressure dependence
Thickness dependence
Iron
Potassium chloride

ABSTRACT

The density functional theory calculated pressure-dependent shear strength S of a four-layer slab of KCl on a Fe(1 0 0) substrate is compared to previous calculations for a bilayer slab to gauge the effect of film thickness on the shear properties of the film. It is found that the shear strength varies with pressure as $S = S_0 + \alpha P$, where P is the contact pressure. The resulting calculated values for the four-layer slab are $S_0\langle 1\,0\rangle = 62 \pm 15$ and $S_0\langle 1\,1\rangle = 65 \pm 11$ MPa while $\alpha\langle 1\,0\rangle$ and $\alpha\langle 1\,1\rangle$ are 0.06 ± 0.01. The values are very close to those calculated for the bilayer slab of $S_0\langle 1\,0\rangle = 64 \pm 9$ and $S_0\langle 1\,1\rangle = 69 \pm 8$ MPa and $\alpha\langle 1\,0\rangle$ and $\alpha\langle 1\,1\rangle$ of 0.05 ± 0.01, and in reasonable agreement with the experiment values. These results suggest that the thickness of the film does not have a profound effect on the shear properties.

1. Introduction

We have shown previously that the pressure-dependent shear properties of a thin, model boundary layer film consisting of KCl on iron can be calculated using first-principles density functional theory (DFT) [1]. First, in order to calculate the shear strength in the absence of an external load, three layers of KCl were placed on a seven layer thick iron slab [1] and the sliding potential was calculated using DFT by laterally displacing the outer layer of the KCl film and then allowing all of the other atoms in the slab to relax to their minimum energies. It was found that shear occurred at the KCl/Fe interface [1]. Thus, since the KCl slab moved rigidly with respect to the iron substrate, the height of the sliding potential for KCl on iron could be obtained without performing a full sliding calculation by simply calculating the energy of the slab located on various high-symmetry points on the surface, thereby resulting in a significant saving in computation time [1]. This simplification occurred because the shear force required to initiate sliding was much lower than the shear modulus of the halide film, with the result that the film was only minimally distorted during sliding, resulting in a shear plane located at the iron–KCl interface [1].

It has been shown experimentally in several cases that the shear strength varies linearly with contact pressure P and can be written as $S = S_0 + \alpha P$, where S_0 is the shear strength at zero pressure and α is a proportionality constant [2–13]. Similar results have been found for the shear of bulk materials [14]. In particular, it was found experimentally, from friction measurements of a thin film of KCl on metal surfaces, that $S_0 = 65 \pm 5$ MPa and $\alpha = 0.14 \pm 0.02$ [15]. The experimental measurements were carried out for KCl deposited onto various metal substrates in ultrahigh vacuum where the background pressure was $\sim 1 \times 10^{-10}$ Torr. This ensured that the system was free of contaminants and that the frictional data were measured for a clean, continuous KCl film on an atomically clean metal substrate [15]. The metal foil substrates were all cleaned in ultrahigh vacuum and their cleanliness measured *in situ* using Auger spectroscopy ensuring that the initial substrates were also clean prior to KCl deposition. While the metal foil substrates were initially likely to be rather disordered, following the cleaning and vacuum annealing process, they are likely to become more ordered [16]. KCl is not used commercially as a boundary film, but it was chosen as a model since it is sufficiently simple that it is amenable to analysis by high-level, first-principles quantum calculations.

Based on the work discussed above for KCl on an iron substrate, it was subsequently possible to obtain a theoretical value of the pressure-dependent shear strength of a composite iron–KCl–iron sandwich by calculating the energy of the system as a function of applied pressure for various locations of the KCl slab with respect

* Corresponding author. Tel.: +1 414 229 5222.
E-mail address: wtt@uwm.edu (W.T. Tysoe).

0043-1648/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.wear.2011.09.008

to the iron substrate, rather than having to carry out a more complex calculation in which the film was sheared while simultaneous imposing a normal load [17]. The calculation was carried out for two layers of KCl sandwiched between iron. The pressure dependence of the shear strength was calculated by compressing the slab from its equilibrium thickness and by plotting the energy of the system as a function of the thickness of the iron–KCl–iron composite film. The energy was found to vary parabolically with film thickness and so was found to deform elastically over the range of pressures used in the experiment [15]. The normal pressure applied to the film was calculated from the first derivative of the plot of energy *versus* normal displacement. It was found that the resulting pressure dependence of the shear strength contained both linear (P^1) and quadratic (P^2) terms. The first pressure-dependent term arose from different equilibrium thicknesses of the film located at different positions on the substrate. This required additional work to be expended against the applied normal load, leading to a shear strength that depended linearly on pressure, in accord with the conclusions of previous work [2–8]. The second term arose from the slightly different compliances of the film located on different sites and resulted in a quadratic pressure dependence in the shear strength. It was found that this effect was much smaller than the one that resulted in the linear pressure dependence, thus proving a fundamental theoretical understanding of the experimentally observed linear dependence. The DFT calculations for a KCl bilayer sandwich gave $S_0\langle 1\,0\rangle = 64 \pm 9$ and $S_0\langle 1\,1\rangle = 69 \pm 8$ MPa, both in excellent agreement with experiment [17]. However, this calculation also predicted that both $\alpha\langle 1\,0\rangle$ and $\alpha\langle 1\,1\rangle$ had values of 0.05 ± 0.01 [17], somewhat lower than the experimentally measured value of 0.14 ± 0.02 [16]. As noted above, for computational economy, the DFT calculations were carried out using a KCl bilayer. One possible explanation for the difference between the experimental and theoretical values of α may be that it depends on the thickness of the KCl film, and this issue is explored in the following sections.

The model for determining the pressure-dependent shear strength exploited the harmonic variation in energy with slab thickness suggested by DFT calculations [2]. Extending this model to explicitly analyze the effect of film thickness on the pressure-dependent shear, the thickness of the film t at some contact pressure P is written as $P = Y(t - t_0)/(t_0)$, where Y is the Young's modulus of the material that forms the boundary film and t_0 is the film thickness at zero pressure. The values of Y and t_0 are obtained directly from the energy change as a function of slab thickness calculated by DFT as shown previously [17]. The shear dependence arises from differences in $t(\Delta t)$ at different locations of the film with respect to the substrate, so that the additional extra work carried out during sliding is $P\Delta t$. If a minimum and maximum in the sliding potential occur at points a and b, respectively, then the change in the film thickness during sliding is $t_b - t_a$. The above equation can be simply rewritten to give $t = t_0 + (Pt_0)/(Y)$. If the corresponding parameters at locations a and b are Y_a and t_0^a, and Y_b and t_0^b, respectively, then:

$$\Delta t = (t_b - t_a) = (t_0^b - t_0^a) + P\left(\frac{t_0^b}{Y_b} - \frac{t_0^a}{Y_a}\right) \quad (1)$$

The values of the film thickness and Young's modulus will vary depending on the location of the slab with respect to the substrate. In the case of KCl on iron, it was found that the energetically most stable – and also the geometrically lowest – site was that in which the potassium and chloride ions were located directly above an iron atom in the substrate. This is contrary to what might be expected based on a hard-sphere model, and arose because of chemical bonding between the iron atoms and the halide ions [1]. If the bonding between the film and the substrate is rather local, the thickness of the film might not be expected to strongly influence t_0 and Y. However, the second term explicitly depends on the thickness of the film. Calculations for the bilayer slab revealed that the second term was much smaller than the first, thereby resulting in an overall linear variation of shear strength with pressure [17]. However, the existence of this term, and the possibility of longer-range bonding interactions warrant an examination of this effect.

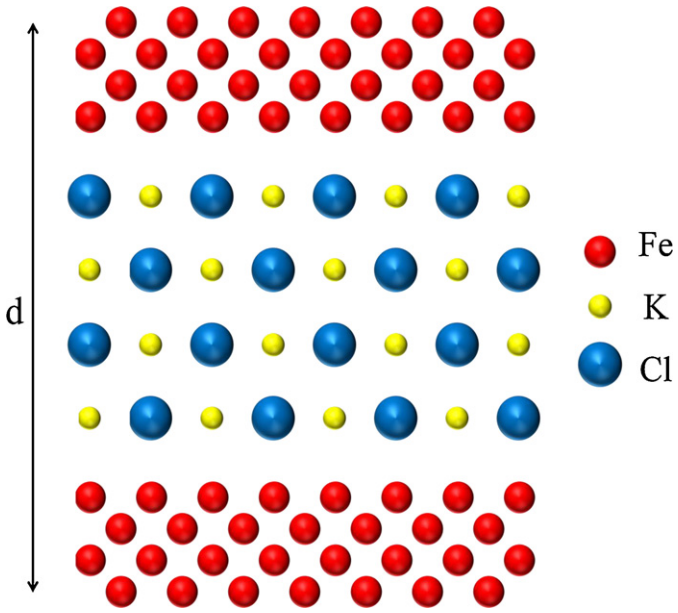

Fig. 1. Depiction of the structure used for the density functional theory calculations showing four layers of KCl sandwiched between iron.

2. Theoretical methods

The KCl/Fe(1 0 0) system was previously modeled using a bilayer of KCl that was placed between Fe(1 0 0) slabs, which are seven iron layers thick [17] and the results are compared in the following to those for four layers of KCl placed between Fe(1 0 0) slabs. The calculations are performed for a (2×2) iron substrate cell with KCl placed epitaxially on the substrate and the calculations are carried out using cyclic boundary conditions to mimic an infinite surface. This orientation is chosen since X-ray diffraction measurements of thicker KCl films have shown them to have a (1 0 0) orientation [18,19]. The calculated bulk lattice spacing for KCl of 0.627 nm agrees well with the experimental value of 0.629 nm. The experimental lattice spacing for iron is 0.287 nm, so that the lattice mismatch between KCl and iron is ~11%. It is assumed in the calculation that the KCl film is strained to so that it is epitaxial with the iron substrate and the structure of the iron plus KCl system is optimized to yield the total energy. The structure of the iron–KCl–iron sandwich with four KCl layers used for the calculation is shown in Fig. 1. Thus, the KCl film is strained to accommodate to the underlying iron lattice. Such pseudomorphic growth of strained films has been observed in other systems where the energy gain by forming an epitaxial film is larger than the energy required to strain the lattice. As the films become thicker, the strain energy increases eventually resulting in a loss of epitaxy [20]. It has been shown previously that shear of the KCl/metal slab occurs at the film–metal interface since the shear modulus of the KCl film is larger than the shear strength of the interface [1]. Thus, such a configuration that uses the smallest (2×2) unit cell will lead to the maximum energy change due to shear between the film and substrate. The use of larger substrate unit cells that reduce the strain of the adsorbed film will result in lower heights of the sliding potentials and thus