



Pressure dependence of the interfacial structure of potassium chloride films on iron



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ARTICLE INFO

Article history:

Received 6 July 2015

Received in revised form 27 September 2015

Accepted 29 September 2015

Available online 3 October 2015

Keywords:

Boundary lubrication

Potassium chloride

Molecular dynamics simulations

Pressure dependence

ABSTRACT

Potassium chloride films on a clean iron surface are used as a model system to explore the interfacial structure of the films and the dependence of that structure on film thickness and pressure. The interfacial structure of one-, two-, three- and four-layer films is measured experimentally using low-energy electron diffraction. Those findings are then complemented by molecular dynamics simulations in which the atomic interaction between the film and substrate is tuned to match film thickness-dependent sublimation activation energy obtained from temperature-programmed desorption measurements. The resultant simulation reliably predicts the structure of thicker films and is then used to study the effect of pressure on the distribution of the lattice constant within and between each layer of the potassium chloride films. Findings indicate that both film thickness and pressure affect the structure within the films as well as the degree of registry between the film and adjacent substrate.

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1. Introduction

The registry between a film and substrate has a profound influence on interfacial shear. A film that is in registry with the substrate will result in the largest friction force since all the atoms at the interface will simultaneously surmount the sliding potentials. Conversely, a lack of commensurability between the atoms in the contacting interface would lead to a lower shear strength which does not scale linearly with contact area [1–5]. For thin films, commensurability may be dependent on the thickness of the film and, in the case of confined films, pressure. Therefore, understanding the friction properties of an interface requires first understanding the dependence of film structure on thickness and pressure.

This complex relationship has been explored using a simple alkali halide as a model boundary lubricating film. While alkali halides are not used as commercial boundary films, their structural simplicity and the availability of a wide range of alkali halides with varying lattice constant, along with their chemical inertness make them attractive candidates for fundamental study [6]. In particular, the shear strength S of KCl films has been measured experimentally in ultrahigh vacuum (UHV) where it is found that S varies linearly with contact pressure P : $S(P) = S_0 + \alpha P$ where S_0 and α are constants [7]. Such linear variations in interfacial shear strength as a function of contact pressure are relatively common in tribological systems [8–10]. The specific system explored in the current study is KCl on Fe(100), which is particularly well suited for such research since precise interaction potentials for computational models are already available for alkali halide films and

it is relatively straightforward to prepare well-defined films in ultrahigh vacuum by KCl evaporation.

This model system has previously been investigated using density-functional theory (DFT) calculations of KCl films on an Fe(100) substrate [11]. However, the requirements of using periodic boundary conditions for the calculations necessitated modeling KCl films that were in registry with the iron substrate. Since the lattice mismatch between KCl and the 100 face of iron is significant (~7%), the resulting KCl film is strained. Nevertheless, these calculations revealed a relatively low barrier in sliding the KCl film against Fe(100) of ~0.7 kJ/mol that yielded a calculated shear strength that was in good agreement with experiment. In this case, it was proposed that the pressure-dependent shear strength arose because of the vertical motion of the atoms in the contact as they slid from one stable site to the next over an energy barrier, analogous to the barrier height in the Prandtl–Tomlinson model for sliding friction [12–17]. However, the low value of the sliding potential implies that the KCl film does not have a strong site preference on the Fe(100) substrate suggesting that KCl might not, in fact, be in registry with the Fe substrate and also emphasizes the need for accurate potentials to describe sliding friction.

Although these results show that the previous DFT calculations yield a potential barrier that is in good agreement with the experimentally measured shear strength for KCl films, there are limitations to the predictions that can be made using this approach given the relatively small simulation size and required periodic boundary conditions which force registry. This suggests the use of molecular dynamics (MD) simulations, which have been extensively used to explore the structural and tribological properties of sliding solid–solid interfaces [18–25]. Such simulations have proven extremely useful in helping to understand the behavior of buried interfaces that, in most cases cannot

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be interrogated directly. However, MD simulations often use generic interface potentials that have been optimized to provide reasonable agreement with the experimental results for a wide range of materials, rather than precisely mimicking the behavior of a specific material. When the interfacial structure is controlled by small energy differences, as is the case in the KCl–Fe system, this may result in the prediction of erroneous structures and the resulting properties. Since it is not generally possible to experimentally interrogate the buried sliding interface, the results of such simulations cannot be directly compared with experiment except to compare predicted parameters such as friction force with the experimental value. It is therefore desirable to tune the interaction parameters in the MD simulation to reproduce experimentally measurable film properties measured for the film–surface interface and then use the tuned simulation to provide information about that interface not available via experiment. This is the approach taken in this work. We adjust the interaction potentials between a model alkali halide boundary film on an Fe(100) substrate by comparison with the results of temperature-programmed desorption (TPD) experiments of the desorption behavior of the films. The structure of thin KCl films is then further characterized experimentally using low-energy electron diffraction (LEED) [26] measurements. Finally, the MD simulations, with interaction potentials fitted to the TPD data, are used to explore the influence of contact pressure on the interfacial structure.

2. Methods

2.1. Experimental methods

LEED and TPD measurements were carried out in a UHV chamber operating at a base pressure of $\sim 1.3 \times 10^{-8}$ Pa following bakeout. The chamber was pumped by means of a liquid-nitrogen-trapped diffusion pump, and the chamber contained a double layer of μ -metal, to minimize extraneous magnetic fields inside the vacuum chamber. The Fe(100) single crystal (Princeton Scientific, 99.999%) purity was initially treated by heating in a hydrogen atmosphere under a pressure of 1 atm at 800 K for ~ 420 h to reduce the level of bulk carbon in the sample. The sample was then attached to the end of a co-axial sample manipulator, and could be resistively heated to ~ 900 K or cooled to ~ 80 K by contact with a liquid-nitrogen filled reservoir. The sample temperature was measured by means of a chromel/alumel thermocouple spot welded to the edge of the sample. The sample was then cleaned by repeated argon ion bombardment cycles ($4 \mu\text{A}/\text{cm}^2$ with a beam energy of 0.5 keV) at an elevated sample temperature (600–700 K) followed by annealing (800–900 K). Auger spectroscopy showed that the iron single crystal was clean after this procedure and exhibited a sharp LEED pattern indicating that the surface was well ordered.

Potassium chloride was evaporated from a small (~ 1 mm internal diameter) alumina tube furnace and the KCl temperature monitored by means of a chromel/alumel thermocouple placed in the KCl pellet to ensure a reproducible evaporation rate, which was monitored by means of a water-cooled, quartz–crystal microbalance in the UHV chamber. The microbalance was mounted to a z-motion drive to allow it to be moved to the same location as the Fe(100) sample to ensure identical KCl fluxes during both source calibration and sample dosing. KCl was deposited with the sample temperature held at ~ 500 K to provide a uniform KCl film [27].

LEED patterns were collected using a four-grid LEED system (Varian) and recorded with a digital camera. Since KCl is susceptible to electron beam damage where the halide ions are removed via a Knotek–Fiebelman [28,29] mechanism in which a core hole in the halide ion created by the incident electron beam decays to emit an Auger electron, thereby creating an unstable Cl^+ ion, all LEED measurements were made using beam energies that were below the Cl 1s ionization energy.

Temperature-programmed desorption (TPD) data were collected using a heating rate of 5 K/s and desorbing species were detected using a (Hiden) quadrupole mass spectrometer whose ionizer was placed in-

line-of-sight of the front face of the sample. Both the sample temperature and the ion intensity were collected simultaneously and exported in Excel format. The desorption data were numerically fit to a rate equation of the form $\frac{d\theta}{dt} = -A \exp\left(\frac{E_{act}}{RT}\right) \theta^n$, where A is a pre-exponential factor, E_{act} is the desorption activation energy, θ is the KCl coverage and n the reaction order, using the experimental heating rate. The rate equation was numerically integrated with temperature steps that were sufficiently small (0.5 K) to yield results that were independent of choice of the temperature step. The parameters were varied to reproduce the experimental desorption maxima and the peak widths and shapes.

2.2. Molecular dynamics simulations

Two computational models were created as shown in Fig. 1. Both models contain an Fe substrate with dimensions of $12.0 \times 12.0 \times 0.6 \text{ nm}^3$. A small slab of an m -layer ($m = 1, 2, \dots, 14$) KCl film with in-plane dimensions of $4.72 \times 4.72 \text{ nm}^2$ was placed in the center of the Fe. In Model 1, shown in Fig. 1(a), the top surface of the KCl was free. In Model 2, shown in Fig. 1(b), a rigid Fe plate, with the same orientation as the bottom Fe surface, was placed on top of the KCl film. During the simulation, the outermost atomic layer of Fe was held fixed. In both models, periodic boundary conditions were applied in the plane parallel to the Fe–KCl interface. Both models were equilibrated by running dynamics for 0.5 ns until the potential energy of the system reached a constant value. Then, the KCl lattice was characterized throughout the film by measuring the distance between all adjacent K (or Cl) atoms in each KCl layer, and then fitting the distribution of the data to a Gaussian function to obtain the mean lattice constant (for the standard unit cell of the NaCl (B1) structure) and its standard deviation. Model 2 was used to investigate the effect of pressure with normal loads of 0.014, 0.14, 1.41 and 14.1 nN applied to the top plate, corresponding to contact pressures of 0.63, 6.30, 63.0 and 630 MPa. The system was equilibrated for 1 ns after each load was applied. We partially validated this model by calculating the Poisson's ratio and elastic modulus from the change in the normal and in-plane dimensions of the innermost four layers of the 8-layer KCl model due to an increase in pressure from 6.3 to 630 MPa. The model predicted a Poisson's ratio of 0.194 and an elastic modulus of 44.8 GPa, which are reasonably consistent with the bulk properties of KCl (Poisson ratio = 0.216; elastic modulus = 38.2 GPa).

The desorption activation energy (E_a) was calculated using Model 1 from the difference in potential energy of the system before and after removing a single KCl pair. E_a was calculated using the equation [30]: $E_a = E_{N-1, \text{KCl-Fe}} + E_{1, \text{KCl}} - E_{N, \text{KCl-Fe}}$, where $E_{N, \text{KCl-Fe}}$ and $E_{N-1, \text{KCl-Fe}}$ are the potential energies of the system before and after the removal of KCl, respectively, and $E_{1, \text{KCl}}$ is the energy of one KCl at equilibrium. The values of $E_{N, \text{KCl-Fe}}$ and $E_{N-1, \text{KCl-Fe}}$ were calculated directly from the simulation after energy minimization. However, this approach could not be applied to $E_{1, \text{KCl}}$ because the empirical potential was fit to crystalline KCl and therefore not expected to be able to predict gas-phase energies, which is the state of the KCl as it is desorbed in the experiment. To address this, we assumed that E_a from MD and experiment should be the same for sufficiently large films, i.e. where the Fe interaction has no effect on activation energy, and the value of the calculated $E_{1, \text{KCl}}$ was adjusted such that the activation energy of the 2.5 nm thick film was the same in the experiment and simulation. We initially tested removing KCl from four different positions on the film, i.e. film center, edge center, and the K- and Cl-terminated corners; see Fig. 1(a). The results showed that, for any film thickness, the smallest E_a was always calculated from the model where we removed KCl from one of the two corners. This is consistent with $\frac{1}{2}$ order dependence of the activation energy from the TPD experiment (see below) which suggested atoms were removed from the edge of the KCl slab. Therefore, in subsequent calculations, E_a was identified as the smaller of the values calculated from the two corner positions.

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