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Structure, magnetism, and adhesion at Cr/Fe interfaces from density functional theory

Donald F. Johnson [a], D.E. Jiang [b], Emily A. Carter [c,*]

[a] Department of Chemistry, Princeton University, Princeton, NJ 08544, USA
[b] Oak Ridge National Laboratory P.O. Box 2008, MS-6201, Oak Ridge, TN 37831, USA
[c] Department of Mechanical and Aerospace Engineering and Program in Applied and Computational Mathematics, Princeton University, Princeton, NJ 08544-5263, USA

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Abstract

Properties of the Cr(100)/Fe(100) and Cr(110)/Fe(110) interfaces are investigated with spin-polarized density functional theory within the generalized gradient approximation (DFT-GGA) for electron exchange and correlation. Contrary to earlier predictions for a monolayer of Cr on bulk Fe, we find intermixing of Cr and Fe at the interface of thick films to be endothermic; hence here we focus on characterizing abrupt, unalloyed interfaces. The ideal work of adhesion for both the (100) and (110) abrupt interfaces is predicted to be $\sim$5.4 J/m^2. We propose that this anomalously strong adhesion between heterogeneous interfaces is derived from significant spin correlations and d–d bonding at the interface.

Keywords: Metal–metal magnetic thin film structures; Metal–metal interfaces; Density functional calculations; Adhesion; Iron; Chromium; Coatings

1. Introduction

Chromium is used as a protective coating on steel in many areas of industry due to its high melting point and wear resistance. For example, steel gun barrels are subjected to extreme operating conditions during firing, such as high pressures, high temperatures, mechanical stresses, and corrosive blast gases [1]. Steel alone will erode rather quickly under these conditions and alloying the steel is not enough to withstand the high temperatures and corrosive gases. Currently, the Army protects the inside of gun barrels with a thin coating of Cr. While the Cr layer provides good thermal protection and adheres strongly to steel, this coating still presents some drawbacks. The electroplating process used to deposit the Cr leaves behind small micro-cracks which allow blast gases to penetrate through, corrode the steel, and erode the interface, leading to spallation of the Cr layer [1]. This damage necessitates frequent maintenance that affects Army logistics. After spalling, the Cr is swept out of the gun tube during subsequent blasts, which leads to another problem: environmental contamination. In an oxidizing environment, Cr will eventually become Cr(VI), which leads in turn to the formation of toxic and carcinogenic chromates in the soil [2,3].

The search for potential alternative protective coatings for steel has been aimed primarily at ceramic coatings/liners (see, e.g. [4] and references therein). Ceramic/iron interfaces have been studied experimentally, e.g., alumina growth on Fe(110) [5] and MgO/Fe [6]. First principles quantum mechanics has been used by our group and others to characterize metal–carbide and metal–silicide ceramic/iron interfaces (e.g., ZrC [7], TiC [8–10], and $MoSi_2$ [11] on Fe substrates).

While ceramics are promising in terms of hardness and thermal protection potential, it is not clear whether they will bond to the steel strongly enough to withstand the

* Corresponding author. Tel.: +1 609 258 5391; fax: +1 609 258 5877.
E-mail address: eac@princeton.edu (E.A. Carter).

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mechanical shocks and stresses associated with the firing of a projectile. As a baseline point of comparison during the search for alternative coatings that adhere strongly to steel, it is important to investigate the very stable Cr/Fe interface currently employed, in order to discern the origin of its strong adhesion. Such insights may help in the design of less toxic, more robust, alternative coatings.

In addition to coatings applications, Cr–Fe interfaces also garner attention from the electronics industry, since the junction of ferromagnetic (FM) Fe with anti-ferromagnetic (AF) Cr exhibits giant magnetoresistance (GMR). Fe/Cr/Fe sandwiches have become a prototype system for studying this effect. Recent DFT calculations predicted that GMR in Fe/Cr/Fe sandwiches is affected by the FM layer thickness [12,13]. The magnetic ordering of Cr ultrathin films on an Fe substrate has been probed by using surface-sensitive techniques, including spin-polarized electron-energy-loss spectroscopy [14] and spin-polarized electron emission spectroscopy [15], with both probes detecting AF coupling at the interface. A monolayer of Cr on an Fe substrate has been examined using spin-polarized DFT within the generalized gradient approximation (GGA) [16,17] and the interface Green's function technique [18], with both methods predicting AF coupling of the Cr monolayer to the Fe substrate, in agreement with experiment. From a structural standpoint, DFT calculations [16,17], Auger-electron spectroscopy [19,20], and scanning tunneling microscopy [21] all have provided evidence of Cr–Fe alloy formation for ultrathin ($\leqslant$1 ML) Cr films on Fe. Semi-empirical tight-binding (SE-TB) calculations predicted Cr–Fe intermixing to be favorable in thicker ($\sim$6 ML Cr) films for certain magnetic configurations [22], but to our knowledge no first principles calculations have investigated thicker films until the present work. Epitaxial growth of Cr on Fe (0 0 1) carried out at elevated temperatures ($\sim$300 °C) does lead to intermixing, however this may be kinetically driven since such intermixing is suppressed somewhat at lower temperatures [20]. Here we employ DFT to investigate properties of both abrupt and alloyed Cr/Fe interfaces in thick films.

2. Calculational details

We performed plane-wave-based, spin-polarized periodic DFT calculations with the Vienna *ab-initio* simulation package (VASP) [23,24]. The all-electron (frozen core) Projector Augmented Wave (PAW) DFT method was employed [25,26]. The GGA of Perdew, Burke, and Ernzerhof (PBE) was utilized for the exchange-correlation functional [27]. We used the standard versions of the PAW-PBE potentials for Fe and Cr supplied with VASP. The PAW method was employed instead of a pseudopotential technique because it has been shown recently that conventional spin-neutral ultra-soft pseudopotentials (USPPs) produce the wrong ordering of some magnetic states of bulk Fe [28,29], while the PAW potentials produce the correct ordering of states. Similarly, the GGA for the electron exchange-correlation functional was used because the local density approximation (LDA) predicts the wrong ground state for Fe (hcp instead of bcc) [28,30].

We performed calculations on two bcc Cr/bcc Fe interfaces: (1 0 0)/(1 0 0) and (1 1 0)/(1 1 0). We did not consider the bcc Fe(1 1 1) surface, since it has a significantly higher surface energy and therefore is less likely to be present as a facet on a polycrystalline substrate during Cr deposition. We increased the k-point sampling for bulk and interface cells until the total energy was converged to within 5 meV/atom. For bulk Fe and Cr, we used a $15\times15\times15$ k-mesh on the primitive 2-atom bcc unit cell to obtain lattice constants and bulk magnetic moments. We used a $15\times15\times1$ k-mesh for the (1 0 0) interface, resulting in a k-point spacing of 0.1478 Å^{-1} in the periodic x- and y-directions. A k-mesh of $15\times11\times1$ was employed for the (1 1 0) interface producing a k-point spacing of 0.1478 Å^{-1} in the x-direction and 0.1425 Å^{-1} in the y-direction. The kinetic energy cutoff for the plane-wave basis was increased until the total energy was converged to within 1 meV/atom. As a result, in all calculations, we used kinetic energy cutoffs of 400 eV for the pseudowavefunctions and 511 eV (402 eV) for the Fe and Fe/Cr (pure Cr) augmentation charges.

The atoms were relaxed to within a force tolerance of 0.05 eV/Å using a conjugate-gradient algorithm. In order to obtain accurate forces, the first-order Methfessel–Paxton method [31] was used for Fermi-surface smearing with a smearing width of 0.1 eV. The error introduced in the total energy (extrapolated to 0 K) by this small smearing width is less than 1 meV/atom.

Using these parameters at the PAW-GGA level of theory, we obtain good agreement with experiment for bulk properties of FM bcc Fe and AF bcc Cr. The predicted equilibrium lattice constant for Fe is $a_0 = 2.834$ Å, the predicted bulk modulus is $B = 174$ GPa, and the predicted local magnetic moment is $\mu = 2.20\ \mu_B$. These values agree well with previous PAW-GGA results [28] and experiment ($a_0 = 2.86$ Å [32]; $B = 168$ GPa, $\mu = 2.22\ \mu_B$ [33]). The equilibrium lattice constant for bcc Cr is calculated to be 2.855 Å and the predicted bulk modulus is 190 GPa, both of which agree fortuitously well with experiment: $a_{exp} = 2.88$ Å and $B_{exp} = 191$ GPa [34]. The agreement must be considered fortuitous because the actual magnetic ground state of bcc Cr is an incommensurate AF spin-density wave (SDW), with a period of 20.83 lattice constants and amplitude $M_{exp} = 0.62\ \mu_B$ [34], which we simplified to the related AF state of bcc Cr. A first-principles calculation of the full SDW would require both a prohibitively large periodic cell as well as a non-collinear-spin DFT calculation [35–37], which is beyond the scope of this work. More importantly, when Cr is deposited on bcc Fe substrates, it is known to undergo spin ordering such that the SDW disappears and the AF Cr magnetic state becomes the preferred state [14]. Since we are primarily interested in the properties of the Fe–Cr interface, the AF state of Cr is of greater relevance. Our AF bcc Cr model has a magnetic moment of