

Surface Science 501 (2002) 261-269



www.elsevier.com/locate/susc

# First-principles study of metallic iron interfaces

A. Hung <sup>a</sup>, I. Yarovsky <sup>a,\*</sup>, J. Muscat <sup>b</sup>, S. Russo <sup>a</sup>, I. Snook <sup>a</sup>, R.O. Watts <sup>c</sup>

<sup>a</sup> Department of Applied Physics, RMIT University, GPO Box 2476V, Melbourne, Victoria 3001, Australia <sup>b</sup> CSIRO Minerals, P.O. Box 312, Clayton South, Victoria 3169, Australia <sup>c</sup> BHP Billiton, 600 Bourke Street, Melbourne, Victoria 3001, Australia

Received 17 July 2001; accepted for publication 29 October 2001

#### Abstract

Adhesion between clean, bulk-terminated bcc Fe(100) and Fe(110) matched and mismatched surfaces was simulated within the theoretical framework of the density functional theory. The generalized-gradient spin approximation exchange-correlation functional was used in conjunction with a plane wave-ultrasoft pseudopotential representation. The structure and properties of bulk bcc Fe were calculated in order to establish the reliability of the methodology employed, as well as to determine suitably converged values of computational parameters to be used in subsequent surface calculations. Interfaces were modelled using a single supercell approach, with the interfacial separation distance manipulated by the size of vacuum separation between vertically adjacent surface cells. The adhesive energies at discrete interfacial separations were calculated for each interface and the resulting data fitted to the universal binding energy relation (UBER) of Rose et al. [Phys. Rev. Lett. 47 (1981) 675]. An interpretation of the values of the fitted UBER parameters for the four Fe interfaces studied is given. In addition, a discussion on the validity of the employed computational methodology is presented. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metal-metal interfaces; Adhesion; Density functional calculations; Surface energy; Low index single crystal surfaces; Iron

# 1. Introduction

Adhesion between metallic iron surfaces plays an important role in many industrial processes. For example, metallic iron (Fe) may be extracted from its constituent ores (mainly oxides) via the fluidised bed iron ore reduction process. Such a plant typically consists of a series of fluidised bed reactors that convert iron ore powders to the metallic iron via solid state reduction, using a mixture of reducing gases [1]. The process often suffers from the build-up of deposits, known as accretions, in various parts of the reactors. In addition, component particles may develop a strong tendency to adhere, forming large clumps of material resulting in defluidisation of the bed [2]. A fundamental understanding of the mechanism by which metal and oxide particles adhere as well as identification of the species most prone to severe adhesion is therefore of vital importance.

Molecular simulation is a technique that can provide fundamental understanding of the processes involved in adhesion at the atomic and subatomic (electronic) levels as a complement to experimental work in this area. It is possible to

<sup>&</sup>lt;sup>\*</sup>Corresponding author. Tel.: +61-3-9925-2571; fax: +61-3-9925-5290.

E-mail address: irene.yarovsky@rmit.edu.au (I. Yarovsky).

construct a model interfacial system of any two surfaces with any degree of lattice match or mismatch. It is also possible, in principle, to make arbitrary alterations to the surfaces, for example, to introduce atomic/molecular impurities and incorporate defects, and then to directly investigate their effects on adhesion. Atomic simulation methods have already been successfully applied to investigations of various ceramic and metallic interfaces, such as MgO/Ag [3], Mo/MoSi<sub>2</sub> [4], and NiAl/Cr [5]. The effects of impurities (S, C, N, O, P, etc.) on adhesion between surfaces have also been investigated [6,7].

As a first step towards the realization of a fundamental model of adhesion between a range of metal and oxide surfaces, we investigate the interaction between the ideal, bulk-terminated (100) and (110) surfaces of bcc iron, a component shown to play a significant role in undesirable adhesion phenomena [2]. In particular, it has been found experimentally that the sticking in the iron ore reduction reactors is affected by a combination of several factors, such as the iron morphology, the surface energy of iron, the shape of the particles, the sulfur activity in the gas phase, and the presence of other species in the ore [2].

The ultimate goal of this study is to develop a comprehensive knowledge of the factors influencing adhesion between iron surfaces at the atomic level. This includes surface relaxation and reconstruction phenomena, temperature and pressure effects, impurities and defects, including the adsorption of atoms and molecules on the surface. This initial communication presents the results of an investigation of the relationship between adhesive energy and interfacial separation for the bcc Fe(100) and Fe(110) interfaces, both in epitaxy and in maximum lattice mismatch, within the framework of the density functional theory (DFT) [8,9] and the plane wave-pseudopotential approximation, as implemented in the Vienna ab initio simulation package (VASP) [10-12]. DFT methods have previously been applied to metallic Fe bulk and surfaces, for example, in the study of surface magnetic moments [13], surface relaxation [14], as well as various metallic Fe systems [15], and have been shown to provide results in good agreement with experiment. In this study, both ideally matching and mismatching interfaces were considered in order to cover the end points of the range of adhesion of real surfaces.

The details of the computational procedure as well as the approach developed to simulate the interfaces is described in Section 2. The calculated discrete adhesive energy curves were fitted to the universal binding energy relation (UBER) [16], which has been shown to give a good description of a range of binding phenomena, including surface adhesion. Thus, an interpretation of the values of the fitted parameters obtained for the four different interfaces provides a framework for understanding their adhesion properties. In addition, the fitted UBER for these interfaces may be used to describe interaction potentials in particle dynamics simulations of the fluidised bed reactors [2,17]. A discussion of the values of the fitted UBER parameters as well as their implications for adhesion are discussed in Section 3.

# 2. Theory and methods

### 2.1. Computational details

All calculations were performed using the VASP code, which performs fully self-consistent DFT calculations to solve the Kohn-Sham equations [18] within the local spin density approximation (LSDA), using the functional of Perdew and Zunger [19] (PZ) or the generalized-gradient spin approximation (GGSA), using the functional of Perdew and Wang [20] (PW91). The electronic wave functions are expanded as linear combinations of plane waves, truncated to include only plane waves with kinetic energies below a prescribed cutoff energy  $E_{cut}$ . A delocalised, plane wave basis provides a good representation of metallic systems, due to the delocalised nature of the conduction electrons within the lattice. Core electrons are replaced by ultrasoft pseudopotentials [21] to render the computations tractable as well as to enhance efficiency. k-Space sampling is performed using the scheme of Monkhorst and Pack [22].

Bulk material, surfaces and interfaces are modelled using the supercell approximation, where

periodic boundary conditions are applied to the central supercell so that it is reproduced periodically throughout space. In order to ensure the reliability of the results from the interface calculations, tests were performed to ensure that the energy and bulk properties of Fe in the bcc phase are converged with respect to the main computational parameters, namely,  $E_{cut}$  and k-space sampling, as described in the results section. Both LSDA and GGSA functionals were used to calculate the structure and properties of bulk Fe and the results compared with experimental data. The ultrasoft pseudopotential for Fe, as included in the VASP package, was used for all calculations.

## 2.2. Interface models and the work of separation

Interfaces were modelled using a surface supercell, where the interfacial separation distance is equated with the vacuum layer thickness between image cells adjacent to each other in the z-direction (see Fig. 1). The surfaces were cut from the relaxed bulk bcc Fe, where the lattice parameter  $a_0$  was calculated using the GGSA PW91 functional. Interfaces where there is a perfect lattice match between the two surfaces (i.e. epitaxial interfaces) were modelled using a surface with an even number of atomic layers, while surfaces in maximum lattice mismatch (i.e. where surface atoms of the two surfaces share the same coordinates in the xy



Fig. 1. Interfaces modelled: (100) match, (100) mismatch, (110) mismatch, (110) mismatch. Profiles of the surface unit cells are displayed below each surface supercell model.

plane within the supercell) were modelled using a surface with an odd number of atomic layers (see Fig. 1).

In this paper, we describe the calculations performed for interfaces between ideal unrelaxed iron surfaces, namely, we calculate the so-called *work of separation* ( $W_{sep}$ ), as the first step towards developing more realistic models of adhesion. The concept of the work of separation and the work of adhesion has been introduced by Finnis [23].

The ideal work of separation is the reversible work needed to separate an interface into two ideal free surfaces, where plastic and diffusional degrees of freedom are supposed to be suppressed. While factors such as the plastic and elastic properties of materials, diffusion and surface segregation (which are all temperature dependent) are important in practical attempts to determine the strength of an interface, the work of separation has a special status as an interfacial property because it is fundamental to other mechanical properties, assuming the role of a state function [23]. It can be defined unambiguously for ideal systems and, therefore, can be relatively easily calculated. The energy needed in a cleavage experiment will always differ from the ideal work of separation, but, other things being equal, the greater the work of separation, the greater the energy needed to cleave the interface, i.e. the stronger the practical adhesion [23]. Hence, the work of separation is vital to the quantitative investigation of adhesion.

In terms of the surface and interfacial excess free energies of the materials, the ideal  $W_{sep}$  is given by the Dupre equation [24]:

$$W_{\rm sep} = \sigma_1' + \sigma_2' - \sigma_{12} \tag{1}$$

where  $\sigma'_1$  and  $\sigma'_2$  are ideal surface free energies of the materials 1 and 2, and  $\sigma_{12}$  is the interfacial free energy. Care must be taken to distinguish the work of separation  $W_{sep}$  from the work of adhesion  $W_{ad}$ , which is defined as the energy required to separate two surfaces from the equilibrium separation to infinity, taking full account of all relaxation and diffusion processes.

 $W_{\text{sep}}$  can be calculated directly from the molecular simulation of isolated surfaces and of these surfaces when brought into a close contact to form an interface [23]. Single point energy calculations

at discrete separation distances, d, allow an "adhesive interaction" energy curve  $E_{ad}(d)$  to be obtained as

$$E_{\rm ad}(d) = (E(d) - E(\infty))/A \tag{2}$$

where E(d) is the total computed energy at separation distance d,  $E(\infty)$  is the total energy at infinite separation, and A is the cross-sectional area of interaction. The well depth of this curve,  $E_0$ , is equivalent to the  $W_{sep}$ . In this work, we calculate  $W_{sep}$  for matching and mismatching interfaces of unrelaxed Fe(100) and Fe(110) surfaces.

# 2.3. Adhesive energy and UBER

The calculated adhesion curves were fitted to the UBER [16], which is given by a Rydberg-type function adapted for the case of interfacial adhesion:

$$E'_{\rm ad}(d) = -E_0(1.0 + d^*)e^{-d^*}$$
(3)

where  $E'_{ad}(d)$  is the fitted adhesion interaction energy (2),  $d^* = (d - d_0)/l$  (scaled distance),  $E_0$  is the depth of the adhesion energy well at equilibrium interfacial separation (equivalent to the work of separation  $W_{sep}$ ),  $d_0$  is the interfacial separation at the adhesion energy minimum, and l is the scale factor, which for transition metals may be interpreted as the surface scaling length, and sets the approximate scale for the distance over which electronic forces can act. More generally, however, the scale factor sets the (unscaled) distance between points of extrema along the UBER curve, and varies for different types of interactions (e.g. adsorption and adhesion, cohesion, diatomic binding), as well as interactions between different materials.

We note that the UBER is considered to give a valid approximation to binding in situations where bonding results mainly from overlap of the tails of wave functions [25]. The UBER therefore is not likely to be valid for a proper description of the adhesion of the interface at large separations, where there is negligible surface wave function overlap and van der Waals' interactions will dominate, nor at very low separations (i.e. significantly less than 1 Å), where significant overlap may develop between core states. We therefore

only computed adhesion energies between approximately 1 and 10 Å interfacial separations, where the UBER is assumed to be valid. In addition to the fundamental difficulties of including data points at extreme separations outlined above, values of the adhesion energy calculated outside the prescribed range are likely to be inaccurate within the present computational methodology. This is because core states are approximated using ultrasoft pseudopotentials, and the calculated energetics of interatomic core overlap which occurs at low separations will therefore be incorrect. In addition, DFT, even within the GGSA, is only capable of providing a partial description of the dispersion forces which dominate inter-particle interactions at long range separations [26], although progress has been made in constructing a functional which correctly reproduces van der Waals behaviour for a range of systems, including that between two parallel surfaces [27].

In summary, fitting the calculated energies to the UBER provides a set of values for the key parameters  $E_0$ ,  $d_0$ , and l, which can be used to interpret interfacial adhesion behaviour between two metallic surfaces. Most importantly, for the purpose of making comparisons between the adhesion energetics of different interfaces, the value of  $E_0$  represents the work of separation for a particular interface.

# 3. Results and discussion

# 3.1. Convergence tests

In order to ensure the reliability of the calculations, the total energy  $E_{tot}$  and lattice parameter  $a_0$  of bulk bcc Fe were calculated with respect to plane wave cutoff energy  $E_{cut}$  and k-point sampling. An  $E_{cut}$  of 300 eV and k-point mesh of  $12 \times 12 \times 12$  gave convergence of  $E_{tot}$  and  $a_0$  to  $10^{-4}$  eV/atom and 0.001 Å respectively. Using the converged parameters, the lattice parameter, bulk modulus and magnetic moment were calculated using both the LSDA and GGSA functionals (see Table 1 for comparison with experimental values). It can be seen that the values calculated using the GGSA gave better agreement with known experi-

	LSDA	GGSA	Experimental
$a_0$ (Å)	2.767 (-3.5%)	2.869 (+0.11%)	2.866
B (GPa)	195 (+16%)	140 (-16%)	168
Magnetic moment/atom (µB)	1.98 (-11%)	2.37 (+6.8%)	2.22

 Table 1

 Structure and properties of bulk Fe, using both LSDA and GGSA functionals

The % deviation from known experimental values [29] are shown in parentheses.

mental values than those using the LSDA. In addition, tests revealed that the LSDA incorrectly predicts the fcc Fe phase to be more energetically stable than that of bcc Fe at 0K, while the GGSA correctly predicts the order of stability. This is consistent with previous findings (see, for example, Jansen and Peng [28]).

Surface formation energies of the unrelaxed (100) and (110) surfaces  $(E_{\text{form}})$  were calculated as a function of slab thickness, using a vacuum layer separation of 10 Å, to determine the number of layers in the surface model required for convergence.  $E_{\text{form}}$  is calculated using the expression

$$E_{\text{form}} = [E_{\text{tot}}(\text{slab}) - nE_{\text{tot}}(\text{bulk})]/(2A)$$
(4)

where  $E_{tot}(slab)$  and  $E_{tot}(bulk)$  are the total energies of the slab and bulk, respectively; *n* is the number of bcc Fe unit cells present in the slab; and *A* is the cross-sectional surface area of the slab.

Although 10 Å was arbitrarily chosen as the separation for determining the surface formation energy convergence, it can be seen from the calculated adhesion curves that there is negligible interaction between image supercells at this separation (see Figs. 2–5). It was found that a slab thickness of 12 atomic layers gave an unrelaxed surface formation energy convergence of 0.001  $J/m^2$ . Therefore, 12 atomic layers were used to simulate surfaces in epitaxy, while 13 atomic layers were used for surfaces in mismatch.

A significant problem posed by modelling the interfacial separation by altering the vacuum layer distance is that we are comparing the energetics between supercells of different geometries. This is because it is well known that there are different k-space sampling requirements for different supercell geometries: in general, a larger cell requires less k-points. Our specific concern was that a cell which has a smaller vacuum layer in the z-direction requires more k-points to be sampled in the z-

direction. Surface supercells with a large vacuum separation in the z-direction requires only one kpoint along this axis. However, in this case, the vacuum separation is gradually reduced, and the system begins to resemble the bulk at lower separations. Thus it is likely that more than one kpoint is required along the z-direction at these separations. For the purposes of making direct comparisons between different supercells, however, it is desirable to use a *consistent* set of parameters throughout this study. While it would be ideal to use, for example,  $12 \times 12 \times 12$  k-points for all surface calculations, we have performed tests which show that the enhancement in numerical accuracy is negligible in comparison with the greatly increased computational demand brought about by using such a large number of k-points when compared to results acquired using a  $12 \times$  $12 \times 1$  k-point mesh. In particular, the  $E_{tot}$  of a 12 atomic layer surface supercell with no vacuum layer separation (i.e. a bulk system) was calculated using both  $12 \times 12 \times 1$  and  $12 \times 12 \times 12$  k-point mesh, and the values calculated using both meshes were found to differ by less than  $10^{-4}$  eV/atom. Thus, a  $12 \times 12 \times 1$  k-point mesh was determined to be sufficient for the present study, and was therefore used for all subsequent surface calculations.

# 3.2. Fe interfaces

The calculated adhesion curves with the fitted UBER functions are presented in Figs. 2–5, grouped according to surface facet (Figs. 2 and 3) and lattice match and mismatch (Figs. 4 and 5). The fitted UBER parameters  $E_0$ ,  $d_0$  and l for the four interfaces are presented in Table 2.

The  $R^2$  values for all of the fitted UBER curves are reasonably high (>0.99), and suggest that the UBER provides a good description of adhesion for



Fig. 2. Adhesion curves for (100) interfaces and fitted UBER.



Fe(110) Match/Mismatch

Fig. 3. Adhesion curves for (110) interfaces and fitted UBER.



Fig. 4. Adhesion curves for matching interfaces and fitted UBER.

all the interfaces within the separation range of 1-10 Å.

It can be seen that the equilibrium separation  $d_0$ for the (100) matching interface is approximately half that of the lattice parameter (2.866 Å); similarly,  $d_0$  calculated for the (110) matching interface give a value of around half the lattice constant



Fig. 5. Adhesion curves for mismatching interfaces and fitted UBER.

Table	2							
Fitted	UBER	parameters	for	(100)	and	(110)	matching	and
misma	atching i	nterfaces						

	(100) matching	(100) mismatch- ing	(110) matching	(110) mismatch- ing
$E_0 = W_{\text{sep}}$ $(J/\text{m}^2)$	4.690	1.422	4.494	2.795
$\gamma$ (J/m <sup>2</sup> )	2.345	N/A	2.247	N/A
$d_0$ (Å)	1.390	2.427	1.991	2.427
l (Å)	0.600	0.567	0.590	0.588
$R^2$	0.99	0.99	0.99	0.99

of the Fe(110) crystal (4.054 Å). For both (100)and (110) mismatching interfaces,  $d_0$  approximately equals the length of the Fe-Fe bond in bcc Fe (2.482 Å). Small variations between the  $d_0$ values acquired from the fitted UBER and their "expected" values are due to the fact that the electron density which minimizes the bulk lattice constant is not exactly the same as that which minimizes the interfacial separation [30]. For all of the interfaces studied, at around 4 Å, non-chemical interactions begin to dominate; each surface interacts with the other as an averaged field. The PW91 functional has been shown to only partially account for long range, dispersion interactions. Thus, for the purposes of elucidating the mechanism of the *initial* stages of particle adhesion, where the particles are separated by a relatively large distance, a computational method which does describe dispersion forces is required for determining the energetics of interfacial interactions at separations far beyond 10 Å, such as classical forcefield methods employing potentials which explicitly include van der Waals terms.

The scale length l calculated for all of the interfaces lie in the range of 0.56–0.6 Å. These values are consistent with the empirically estimated value of 0.56 Å, which represents the average surface screening length of several Fe surfaces [16].

The  $W_{sep}$  value for the (100) matching interface is higher than that of the mismatching interface by approximately 70%. This can be explained on the basis of the dominant Fe-Fe interactions at the respective interfaces. At the equilibrium separation, the (100) mismatch interface can approximately be described as having one nearestneighbour interaction per surface unit cell (each top layer Fe atom of one surface directly faces, and is 1-fold coordinated to, an atom at the other surface at a separation of 2.42 Å, over an area of 8.21  $Å^2$ , the surface area of a (100) surface unit cell). The (100) epitaxial interface can approximately be described as having four nearest-neighbour interactions and one next-nearest-neighbour interaction, over the same surface area (each top layer Fe atom of one surface is 4-fold coordinated to top layer atoms of the other surface at 2.42 Å; in addition, each surface atom interacts with an atom at the second atomic layer of the other surface, at 2.866 A; these interactions occur over an area of 8.21  $Å^2$ ). Thus, the (100) epitaxial interface may be expected to have a significantly higher  $W_{sep}$  than that of the mismatching interface, the former having "more bonding" over the same surface area.

A similar argument may be applied to the (110)interfaces, for which the  $W_{sep}$  for lattice match is also higher than that of lattice mismatch. The (110) mismatch interface, at equilibrium separation, has one nearest-neighbour interaction per surface unit cell (1-fold coordination at 2.42 Å over 5.80 Å<sup>2</sup>), while the (1 1 0) epitaxial interface has two nearest-neighbour and two next-nearest neighbour interactions per unit cell (4-fold coordination at 2.482 and 2.866 A over 5.80  $A^2$ ). Again, the epitaxial interface may be expected to have a higher  $W_{sep}$ . However, due to the lack of 4-fold nearest-neighbour interaction at this interface, the discrepancy between  $W_{sep}$  of the (110) matching and mismatching interfaces is expected to be somewhat less than that for the (100) facet. Indeed, the lattice match  $W_{sep}$  value for this facet

is only 38% higher than the mismatching value. The similarity of the calculated values of  $W_{\text{sep}}$  for the matching (100) and (110), as obtained in the present study, may also be explained in terms of bonding per unit area at the epitaxial interface of the two surfaces. As noted previously, the (100)epitaxial interface, at equilibrium, consists of four nearest-neighbour interactions over an area of 8.21  $\dot{A}^2$ . The (110) epitaxial interface consists only of two nearest-neighbour and two next-nearest neighbour interactions, but this occurs over a smaller area of 5.80  $Å^2$ . Therefore, the (100) facet consists of a larger amount of interactions dispersed over a wider surface area, while the (110)facet consists of a smaller amount, but which occurs over a smaller surface area, resulting in a similar electron density per unit surface area. This in turn results in the energy required to separate the epitaxial interfaces of these facets to be somewhat similar. If this hypothesis is valid, the same trend should, in principle, occur for the surface energies calculated using the present method for all metallic bcc systems. Calculations of the surface energies of various facets of other bcc metals will need to be performed in order to validate this explanation.

It is of interest to note that the (110) facet is predicted to be slightly more stable than that of the (100) as demonstrated by the calculated (100) $W_{\text{sep}}$  being slightly higher than that of (110). Experiments indicate, however, that the surface energy of the (100) [31] surface is lower than that of the (110) [28,32] surface. We should note that caution must be exercised when making direct comparisons between the results obtained in this study for ideal surfaces and experimentally determined order of surface and interface stability. Real interfaces are anisotropic, and likely to have regions of lattice match and mismatch. Experimental results represent values for such a "mixed" interface and depend on the match-mismatch ratio in every particular case. It is therefore necessary to take into account the contributions from both the matching and mismatching parts of an interface to the interaction potential, and hence the predicted relative surface stabilities.

This point can be illustrated by inspection of the calculated adhesion curves. The (100) mismatch

interface has a significantly lower equilibrium energy well depth (i.e.  $W_{sep}$ ) than that of the (110) mismatch interface (see Figs. 2–5); in addition, the  $W_{sep}$  of the (100) matching interface is only slightly higher than the (110) matching interface. Since the interaction potential of real iron interfaces is likely to be an average of the lattice match and mismatch potentials, this would give an overall lower  $W_{sep}$  value for Fe(100) surface compared with Fe(110), giving an order of stability consistent with experimental findings.

In addition, it should be noted that disagreements exist in the literature regarding the predicted order of stability for these surface facets from computed surface energies using various computational methods. For example, Haftel et al. [33] reported different relative stabilities of the (100)and (110) surfaces when different parameterisations of the EAM potential is used, while the calculations of Tyson and Miller [32] and Vitos et al. [34] gave a relative stability order in agreement with experiment. Again, caution must be exercised in making direct comparisons between results acquired using density-functional methods (as in this study) and that of empirical techniques. Forcefield methods often give results which are not in a good agreement with experimental data that have not been used for the parameterisation of the potentials. For example, in the EAM method of Haftel et al. [33], the potentials employed were parameterised using bulk properties, then directly transferred to surface calculations, which may be a cause for its varying performance.

Furthermore, in real materials formation of an interface and subsequent separation of the newly formed surfaces will result in various dissipative processes at those surfaces—for example, surface relaxation, reconstruction, and diffusion processes [23]. The measured surface energies of real surfaces, after all dissipative processes have run their course, are therefore expected to be lower than those determined from computations on ideal surfaces, where such processes are purposely suppressed. In essence, such calculations may be thought of as being performed on interfaces where the surfaces are separated instantaneously from the equilibrium separation (i.e. the bulk) to infinity, before relaxation and diffusion can take place

and the surface energy values calculated are therefore "instantaneous" surface energies [23]. In addition to variation in the *absolute* values of surface energies between ideal and real systems, the *order of stability* of various surface facets may also be quite different when dissipative processes are taken into account.

# 4. Conclusions

The relationships between the adhesive energy and interfacial separation of the Fe(100) and Fe(110) matching and mismatching interfaces were studied using the density functional-plane wave-pseudopotential (DFT-PW-PP) formalism with the GGSA exchange-correlation functional. The UBER was fitted to the calculated adhesion curves. The values of the parameters extracted suggest the (110) surface to be slightly more stable than that of the (100). However, the order of stability is reversed if the effects of having both matching and mismatching interfaces are taken into consideration, in agreement with experimental findings. The results acquired thus far suggest that the DFT-PW-PP method within the GGSA is a valid approach for determining the adhesion characteristics of Fe surfaces; however, further tests on other surfaces may be necessary to fully justify this assertion.

The work presented in this communication will be extended in several directions. The effects of full relaxation of the Fe surfaces on interfacial adhesion will be investigated. We note that a number of studies have been published on "avalanche" in adhesion-i.e. surfaces collapsing together within a critical separation distance when surface relaxations are incorporated into the simulation (see, for example, Smith et al. [35]). To investigate avalanche in adhesion by the DFT-PW-PP method, we are currently considering the effects of surface relaxation on adhesion over a range of interfacial separations in order to determine the conditions under which avalanche occurs (if at all), as well as consider the adequacy of the UBER representation for fully relaxed surfaces.

In addition, the effects of adsorbates, such as oxygen, phosphorus, carbon and sulfur on the

structure and adhesion of surfaces will be examined. Similar work may be applied in the study of interfaces between other major components in the fluidised bed iron ore reduction (FIOR) process which may contribute to accretion formation.

## Acknowledgements

Useful discussions with Prof. Mike Finnis (Queen's University of Belfast, UK) are thankfully acknowledged. We thank BHP Billiton for their financial support.

# References

- [1] D. Georg, Engineers Australia 72 (6) (2000) 30.
- [2] S. Hayashi, S. Sawai, Y. Iguchi, ISIJ Int. 33 (1993) 1078.
- [3] T. Hong, J.R. Smith, D.J. Srolovitz, J. Adhes. Sci. Technol. 8 (1994) 837.
- [4] T. Hong, J.R. Smith, D.J. Srolovitz, Phys. Rev. B 47 (1993) 13615.
- [5] J.E. Raynolds, J.R. Smith, G.L. Zhao, D.J. Srolovitz, Phys. Rev. B 53 (1996) 13883.
- [6] T. Hong, J.R. Smith, D.J. Srolovitz, Phys. Rev. Lett. 70 (1993) 615.
- [7] J.E. Raynolds, E.R. Roddick, J.R. Smith, D.J. Srolovitz, Acta Mater. 47 (1999) 3281.
- [8] P.A.M. Dirac, Proc. Cambridge Phil. Soc. 26 (1930) 376.
- [9] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864.
- [10] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558;
   G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251.
- [11] G. Kresse, J. Furthmuller, Comput. Mat. Sci. 6 (1996) 15.

- [12] G. Kresse, J. Furthmuller, Phys. Rev. B 54 (1996) 11169.
- [13] A.A. Ostroukhov, V.M. Floka, V.T. Cherepin, Surf. Sci. 333 (1995) 1388.
- [14] T. Kishiabd, S. Itoh, Surf. Sci. 358 (1996) 186.
- [15] J. Izquierdo, A. Vega, L.C. Balbas, D. Sanchez-Portal, J. Junquera, E. Artacho, J.M. Soler, P. Ordejon, Phys. Rev. B 61 (2000) 13639.
- [16] J.H. Rose, J.R. Smith, J. Ferrante, Phys. Rev. B 28 (1983) 1835.
- [17] B.H. Xu, A.B. Yu, Chem. Eng. Sci. 52 (1997) 2785.
- [18] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) 1133.
- [19] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048.
- [20] J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
- [21] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.
- [22] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
- [23] M.W. Finnis, J. Phys.: Condens. Matter 8 (1996) 5811.
- [24] A. Dupre, Theorie Mechanique de la Chaleur, Gauthier-Villars, Paris, 1869.
- [25] A. Banerjea, J.R. Smith, Phys. Rev. B 37 (1988) 6632.
- [26] S. Tsuzuki, H.P. Luthi, J. Chem. Phys. 114 (2001) 3949.
- [27] M. Lein, J.F. Dobson, E.K.U. Gross, J. Comput. Chem. 20 (1999) 12.
- [28] H.J.F. Jansen, S.S. Peng, Phys. Rev. B 37 (1988) 2689.
- [29] H.C. Herper, E. Hoffmann, P. Entel, Phys. Rev. B 60 (1999) 3839.
- [30] A. Kiejna, K.F. Wojciechowski, Metal Surface Electron Physics, Elsevier Science Ltd., Oxford, UK, 1996.
- [31] B.L. Averbach, D.K. Felbeck, G.T. Hahn, D.A. Thomas (Eds.), Fracture, John Wiley Sons Inc., New York, 1959, p. 193.
- [32] W.R. Tyson, W.A. Miller, Surf. Sci. 62 (1977) 267.
- [33] M.I. Haftel, T.D. Andreadis, J.V. Lill, Phys. Rev. B 42 (1990) 11540.
- [34] L. Vitos, A.V. Ruban, H.L. Skriver, J. Kollar, Surf. Sci. 411 (1998) 186.
- [35] J.R. Smith, G. Bozzolo, A. Banerjea, J. Ferrante, Phys. Rev. Lett. 63 (1989) 1269.