A first-principles approach to determine surface stability of Pt and Ir doped on β2 FeAl (011) plane

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Abstract. Ferroaluminum (FeAl) is a ferroalloy metal which usually consists of 40% to 60% aluminium. It is of great applications which include de-oxidation of steel, hard-facing applications, reducing agents, thermite reactions, AlNiCo magnets, and alloying additions to welding wires and fluxes. Herein, to investigate the structure of FeAl mesoscopic crystals segregating in solid state alloys, we have determined their equilibrium structures based on the First-principles approach and molecular dynamics techniques for stoichiometric surface terminations and temperature dependence. Thus, the investigation of surface stability and interaction with either Pt/Ir will provide insights into the strength and oxidation behaviour of the FeAl ternary doped systems. The predicted stable systems showed enhanced stability for corrosion reduction. The alumina layer formed on the metal's surface acts as a good barrier against oxygen penetration, delaying the production of other faster-growing oxides. The major goal of this study is to use coating to increase stainless-steels for high-temperature oxidation resistance.

1 Introduction

There exists three stable surface structures in iron aluminides intermetallic, the Fe: Al=1:1, Fe: Al=1:2 and Fe: Al=1:3 surface structures. Surface properties as resistance to oxidation, adsorption, corrosion, magnetic properties and Gibbs free energy are significantly influenced by surface structures [1]. One of the most applied alloys in corrosion industry is Ferroaluminium (FeAl) with 50:50 composition. It is the most often used stainless steel and is progressively being used in coal-fired boilers, heat pipes, steam turbines, and other applications. It remains a challenging task for researchers to design a FeAl alloy with excellent creep resistance and both low and high temperature ductility for advances towards industrial and economic processing. In such design, it is empirical that the inherent corrosion and oxidation resistance properties be retained during the alloying process. The most effective method for increasing stainless steel corrosion resistance is to put a protective coating to the material's surface. Thus, aluminide coatings have remarkably become the most applied method in protective coatings for Al_2O_3 and possess excellent high-temperature

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corrosion resistance [2]. Corrosion of metals buried in soil and various environmental conditions is influenced by moisture content, dissolved ions, acidity, and the presence of corrosive bacteria. The first two of these characteristics may be determined remarkably well by measuring resistivity.

The surface structures for transition metal aluminides have been studied extensively due to high-temperature applications. Fe-Al has a wide range of phase diagram components and it is one of the simplest intermetallic compounds. Therefore, it was selected to explore the structural properties of ternary alloying as well as the effect of external environment on the structure mechanism [3]. Component coating is one of the techniques used to improve the electrochemical performance and enhance resistance against decomposition of materials. Despite several experimental and theoretical studies addressing the surface coating using β2 FeAl, the reactivity of the material toward the components is not yet fully understood [4].
Irrespective of all the advances in improving the performance and ductility of FeAl, there is still a lack on the systematic mechanism on the influence of ternary alloying on the bulk properties. Hence, it remains a challenging task for researchers to design a FeAl alloy with excellent creep resistance and both low and high temperature ductility for advances towards industrial and economic processing. If a metallic substance does not generate a protective oxide layer on its surface at high temperatures, it loses too much base mass. Thus, it is empirical that the inherent corrosion and oxidation resistance properties be retained during the alloying process. This study investigates the effect of ternary alloying with Pt and Ir on the structural and thermodynamical properties of the β2 FeAl system. Hence, surface structures play an important role in surface properties such as corrosion resistance, oxidation, and adsorption as well as magnetic properties.

2 Computational method

Theoretical studies of solids and surfaces have grown in popularity over the previous 30 years, due to the increasing availability of powerful computers. This has been accompanied by improvements in methodologies.
The bulk FeAl phase calculations were carried out using the Vienna Ab initio Simulation Package (VASP) [5], implemented Metadise to carry out quantum mechanical calculations within the Kohn–Sham (KS) DFT. The Perdew–Burke–Ernzerhof (PBE) version of the generalized gradient approximation (GGA) was employed as the exchange–correlation potential embedded within MedeA environment [6].
Integrations in the reciprocal space were performed using a Monkhorst–Pack grid of 4x4x1 k-points which resulted in electronic and ionic convergence. The k points calculations were determined to have an energy difference within 1 meV per cell. The plane wave cut-off energy was set to 270 eV. The spin polarization was taken into consideration, due to magnetism of iron on the β2 FeAl pristine system. In order to ensure accurate and realistic surface calculations, METADISE code [7] was preferably used since it not only take periodicity in the plane direction into account but also offers the various atomic layer stacking that results in a zero dipole moment perpendicular to the surface plane.

3 Results

3.1 Surface energies

The β2 structure was reported to have two plane modes; NiAl with (100) planes and CoAl with (111) planes. Both deform on the (100) plane which only has 3 independent plane systems and are insufficient to fulfil Von Mises criterion, yet they require five independent

plane systems which are present [8]. Therefore, the (011) surface plane model was chosen, since it has been reported as the dominant stable planer for the β2 FeAl surface simulation.

3.1.1 Bulk and surface models

The crystal structure of β2 FeAl has a cubic symmetry with the space group of Pm-3M. The structure consists of one Fe- and one Al- atom along the [011] as shown in Fig. 1. Following a full bulk optimization, the predicted equilibrium lattice parameters were a = b = c = 2.868Å [9] which is 99 % in agreement with the experimental value of 2.908 Å [10].

The Iron Aluminides (FeAl) surface terminations studied in this work were determined by cleaving a fully optimized (2 × 2) supercell unit cell using the method implemented in the METADISE code [11] to build slab models. We chose to model the (011) surface plane, since it has been reported as the dominant stable planer for the β2 FeAl surface simulation. The surfaces classification of the FeAl system according to Tasker [12] type I, each plane contains an equal number of cations and anions (the net dipole moment is zero; $\mu = 0$). The calculation method of surface energy is a typical slab model. The thickness of vacuum layer is more than 15 Å to ensure the accuracy of surface calculation results, along a with slab thickness of 10 Å.

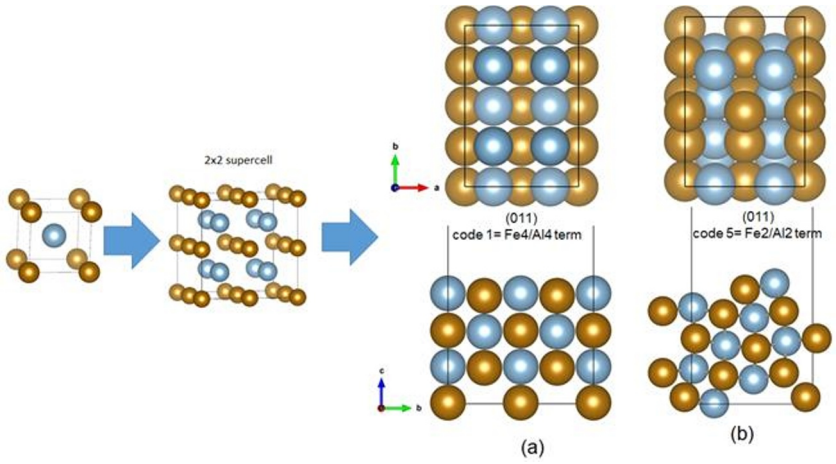

Fig. 1. Side view of the bulk, supercell of the bulk and the (011) terminations from the β2 FeAl surface structure.

The electronic charge transfers between the Fe- termination and Al- termination molecules were investigated. We carried out a Bader charge analysis for the most favorable adsorption configurations found on the β2 FeAl (011) surface. We also explored the effect of surface coverage (θ) on the work function (ϕ) for the Fe- and Al- molecules placed onto the surface.

The largest value of the work function (ϕ) was observed with the value of 4.554 eV on the Fe4/Al4 (011) surface plane. This concluded that this surface plane is the most stable termination with higher work function compared to Fe2/Al2 termination, see Table 1. This implies that if the work function is very low, system is reactive and if the work function is high, the system is less reactive which is the desired outcome. Both Fe-terminated and Al-terminated of FeAl are considered. For elemental materials, surface energies (E_{surf}) are defined according to:

$$E_{surf} = \frac{1}{2A}(E_{tot} - NE_{bulk}) \quad (1)$$

where $\boldsymbol{E_{tot}}$ and $\boldsymbol{E_{bulk}}$ are the total energies of surface system and bulk, and $\boldsymbol{N}$ is the number of bulk unit cells in the slab.

The distribution of Fe- and Al- charges on the surface was taken into consideration to create a stable equilibrium in case the forces acting on the system cause it to shift back to its initial position. Both pristine surfaces plane charges of (011) were determined according to the energy of each slab.

Table 1. The calculated surface energies(γ_r), the atomic charges (q) of Fe- and Al- and the work functions (Φ) of each termination from this work of the (011) FeAl intermetallic.

Surface Termination		γ_r (eV/Å^2)	q(Fe) (e$^-$/atom)	q(Al) (e$^-$/atom)	Φ (eV)
Fe4/Al4	(011)	0.165	1.515	1.823	4.554
Fe2/Al2		0.187	1.504	1.842	4.032

The minimum bond length= 0 and the maximum bond length was between Al:Fe = 2.5 and Al:Pt/Ir = 3.0. The doping transitions metal (Pt/Ir) was gradually increased to observe the surface free energy (SFE) of each concentration, until we had a monolayer on the surface in order to identify the most stable surface. The side view in figure 2a, b clearly illustrates the change in the atomic position and arrangement as doping is gradually increased on the system (top view figure 2a, b). The first doping began from 1 concentration of Pt/Ir up to 4 concentration of Pt/Ir (which is the monolayer).

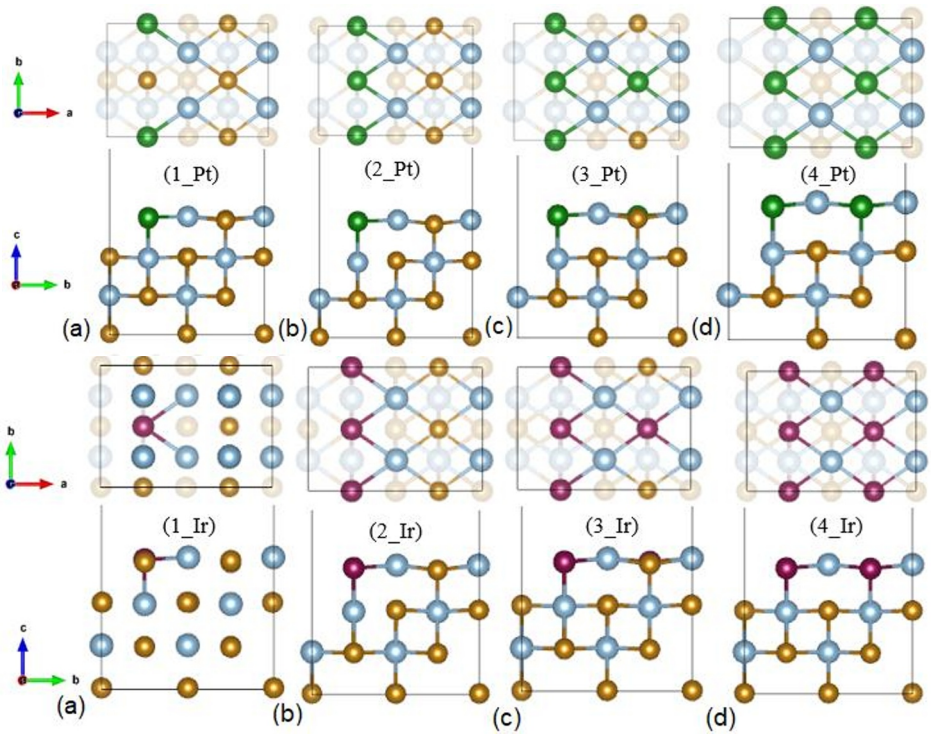

Fig. 2. Top and side view of the four surface layers for the four stable $Fe_{1-X}Pt/Ir_XAl$ (011) surface structures (a) Fe:Al= 1Pt/Ir; (b) Fe:Al= 2Pt/Ir; (c) Fe:Al= 3Pt/Ir; (d) Fe:Al= 4Pt/Ir.

The difference between the active slip directions affected the stability of the intermetallic significantly. We observed that the (011) plane is the most stable surface resulting in the lowest surface energy, followed by (111) plane and least followed by (001) plane.
The magnitude of the surface energy depends on the interaction between the molecules, in this case the SFE is high due to strong metallic bonds between the metal atoms, unlike that of polymers where the molecular forces are typically weaker resulting in low SFE. The Pt and Ir ternary doped systems, showed that Pt is more stable. This is illustrated by lower surface free energies as the concentration of Pt is increased as observed in fig. 3.

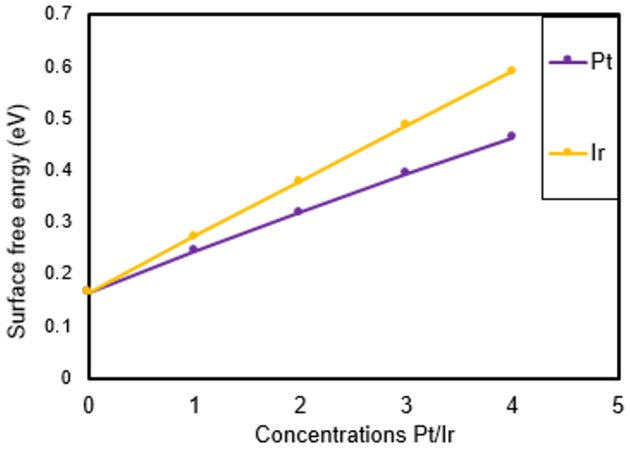

Fig. 3. The calculated surface free energies of the facets with different TM (Pt/Ir) concentrations.

The pristine β2 FeAl system in figure 4a showed electronic instability on the density of states since the fermi level (0 eV) does not fall within the pseudo gap, the high peaks are contributed by the *d*- and *s*- spin up orbital from Fe- and Al- element. Ternary doping with Pt yielded electronically stable systems compared to Ir ternary doped systems (see figure 4b, c). Concentrations of 1 to 3, of Pt doping demonstrated three surface stability, where the pseudo gap is falls within the fermi level. In the case of Ir doped systems, they exhibit high peaks within the fermi level falling outside the pseudo gap (concentrations 1, 3 and 4). However, the 2 Ir concentration was found to be electronically stable surface. Comparing Pt and Ir concentrations, doping with Pt enhanced the surface stability for oxidation reduction for stainless steel component coating.

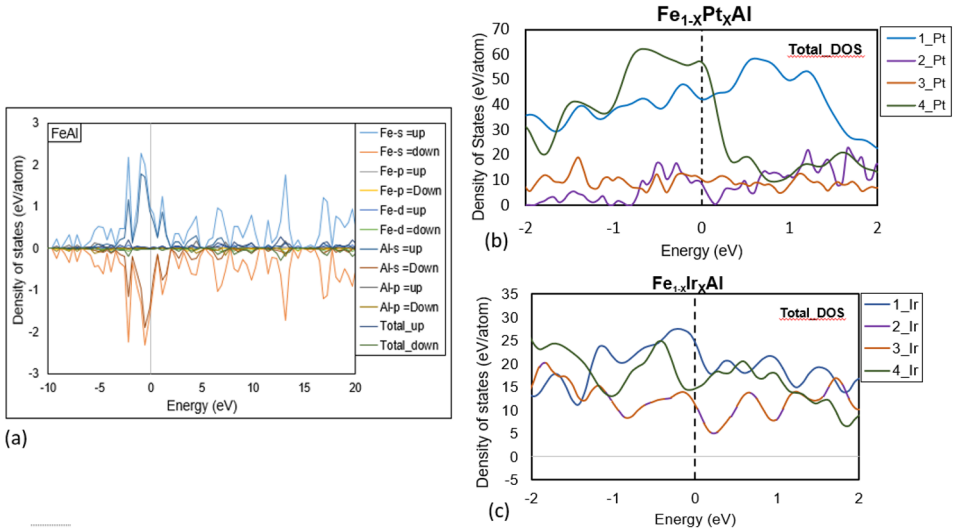

Fig. 4. Density of states of (a) FeAl, (b) $Fe_{1-X}Pt_XAl$ and (c) $Fe_{1-X}Ir_XAl$ with different TM (Pt/Ir) concentrations.

4 Conclusions

In this paper, we have used DFT methods within the GGA approximation to model the 011 surface planar orientation of the β2 FeAl crystal. We have examined the redox characteristics of the most notable surfaces and the stabilities of their non-dipolar stoichiometric surface terminations. We conclude that the Fe- terminated (011) plane is the most stable FeAl surface plane, and thermodynamically favourable in the region of FeAl as the most stable slab model. This agrees with the work function as the Fe4/Al4 slab had the highest work function resulting in less reactive material, in turn reducing the oxidation process implying stability. Thus, ternary alloying enhanced stability of the FeAl 011 surface plane with one most stable slab model. Due to how metals behavior, in terms of the density of states, the conductions occurred in one or more partially filled bands that took properties both from the valence and conduction band resulting from the Fe and Al spin up orbitals. Here in, Platinum and Iridium additions appeared promising for improving the intrinsic surface properties of β2 FeAl alloy because they stabilize the austenitic domain, which allowed to achieve an alpha/gamma in the otherwise totally ferritic Fe-Al alloys. Therefore, the amount of aluminium in iron aluminides is high enough to form a compact, well-adhered Al2O3 resistive coating on the surface for stainless-steel superior protection, durability as well as an authentic appeal for production in component coating.

The calculations were performed at the Materials Modelling Centre (MMC) in the University of Limpopo and the Centre for High Performance Computing (CHPC) in Cape Town. The authors also acknowledge the National Research Foundation (NRF) for their financial support. Advanced Materials Initiative (AMI) and MINTEK are highly appreciated. Acknowledgement and appreciation to Brian Ramogayana for the assistance in the surface work calculations.

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