

# A FIRST PRINCIPLES THEORY OF METAL-CERAMIC INTERFACES

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## ABSTRACT

We discuss the recent first principles calculations of the properties of interfaces between metals and ceramics, with particular reference to electronic structure and adhesion. A consistent picture of the nature of the bonding is proposed via calculations made for metals on MgO and alumina and for metals on SiC.

## INTRODUCTION

It is now clear that some of the most important physical properties of materials in high technology applications are either controlled or are strongly influenced by the presence and properties of interfaces. Among them, the metal-ceramic interfaces are essential in electronic packaging systems, thin film technology, ceramic metal composites. Often the bonding and adhesion between oxide and metal is critical to the performance of a component. Furthermore, novel materials with unique properties may be developed from multilayer ceramic-metal structures.

The study of metal-ceramic interfaces poses some formidable challenges both experimentally and theoretically. These range from the difficulties of interface formation and structure, the nature and role of interdiffusion (and in general of the chemistry) at the interface, the nature and strength of bonding, the work of adhesion, ..., to the complexities of understanding interface failure (e.g., fracture resistance, mechanics of crack propagation).

Yet there is very little theoretical understanding of the strength and chemical nature of the bonding or the atomic structure of the interfaces. At a qualitative level, we can quote approaches which relate interfacial energies to other parameters (e.g. to reaction energies). Such approaches organize data [1-3]. Quantitative theories and predictive models for interface bonding are based mainly on atomistic theories. However the useful concepts for bulk materials, such as the shell model for ionic crystals or the embedded-atom model for metals, are inapplicable at the interface, where the nature of the bonding is in transition. To understand just what does happen at metal-ceramic interfaces, there is an obvious need for first principles calculations of the electronic charge density, the total energy and the relaxed structure. First principles calculations have made enormous progress in recent years due to new algorithms and techniques and to the increase in available computer speed and memory [4-5]. At the hearth of first principles methods is

the time-consuming solution of a Schrödinger equation, which is only possible for systems containing a relatively small number of inequivalent atoms (roughly one hundred). However, by applying periodic boundary conditions, an infinite multilayer arrangement of interfaces can be simulated [5]. The aim of first principles methods is to predict the structure and properties of the interface, both atomic and chemical, without recourse to experimental data to fit parameters in any model. They can also be used to develop intuition about the nature of the bonding and then to lay the physical basis of atomistic models of the metal-ceramic interaction. Simpler models are necessary if larger systems, including misfit dislocations and other defects, are to be simulated, with a view to understanding the atomic processes of growth and failure. The chemistry of impurity segregation and its effect at interfaces is another area in which first principles calculations can contribute.

In this article we review the main theoretical approaches which have been taken and the progress which has been made in understanding metal-ceramic cohesion. But before, we briefly discuss the progress made in rationalizing the data by a judicious combination of thermodynamic data.

### THERMODYNAMIC BACKGROUND

When analyzing data on interface stability, the most discussed quantities are the work of adhesion or the wetting angle. By definition, the work of adhesion is the reversible free energy change for making free surfaces from interfaces, whereby the free surfaces are in equilibrium with the solid (or liquid) and gaseous components. For the ceramic (S)/liquid metal(L)/vapor (V) system, the Dupré equation is:

$$W_{ad} = \sigma_{SV} + \sigma_{LV} - \sigma_{SL} \quad (1)$$

where  $\sigma_{SV}$  is the ceramic surface energy,  $\sigma_{LV}$  the liquid metal surface energy and  $\sigma_{SL}$  the interfacial ceramic-liquid metal energy.

$W_{ad}$  can be evaluated by sessile drop data ( $\sigma_{LV}$  and contact angle  $\theta$  of the metal on the ceramic) using the Young-Dupré equation:

$$W_{ad} = \sigma_{LV} (1 + \cos \theta) \quad (2)$$

Following Tomsia [6] and Finnis [7] it is essential to make a distinction between the work of adhesion,  $W_{ad}$ , and the work of separation,  $W_{sep}$ , for all systems having more than one component. The work of separation is defined as the reversible work needed to separate the interfaces into two free surfaces, a thought experiment whereby diffusional degrees of freedom are supposed to be suppressed. Such a scheme has some consequences for multicomponents systems via the diffusion process of chemical equilibration. Just after the cleavage, the concentration of any segregants at the freshly created surfaces will at first be the same as they were at the interface, but only for an instant: it is the reference state for the work of separation. Then the diffusion occurs and adjust the concentrations to new values corresponding to the equilibrium state of the free surfaces. When these equilibrium values have been reached, the surface energies will

display new equilibrium values: that corresponds to the reference state of the work of adhesion.

An other quantity of interest introduced by Eusthatopoulos and coworkers [8] to correlate the energetical properties of the metal-ceramic ( $\text{Al}_2\text{O}_3$  or SiC) interface with the formation energy of M-O or M-Si systems is the work of immersion:

$$W_i = \sigma_{SL} - \sigma_{SV} \quad (3)$$

and as  $W_{\text{ad}}$ ,  $W_i$  can be evaluated from sessile drop data according to:

$$W_i = -\sigma_{LV} \cos\theta \quad (4)$$

From a theoretical point of view, it is a straightforward thing to calculate  $W_{\text{sep}}$  by comparing the total energy of two systems, one in which the surfaces are free and the other in which they are in contact, forming the interface. A direct calculation of  $\theta$  or  $W_{\text{ad}}$  is more problematic since they require to capture the main features of the equilibrium process, that means the segregation chemistry and thermodynamics in the system.

### AB INITIO METHODS

First principles methods, also referred to as *ab initio* methods, include all the methods of total energy calculations if these do not involve parameter fitting. The most widely used class of methods is based on the density functional theory (DFT) of Hohenberg and Kohn, in the formulation of Kohn and Sham [9], which reduces to the self-consistent solution of a single-particle Schrödinger equation:

$$-\nabla^2 \psi_i(r) + V_{\text{eff}}(r) \psi_i(r) = \varepsilon_i \psi_i(r) \quad (5)$$

The electron density  $n(r)$  is obtained from the solutions as:

$$n(r) = 2 \sum_{i \in \text{occ}} |\psi_i(r)|^2 \quad (6)$$

in which the summation is over all the occupied orbitals and the factor 2 counts the spins. The self-consistency is especially important for systems with sizeable charge transfer between the atomic constituents, which is the case of metal-ceramic systems.

Two implementations of the DFT are classically used for calculating surfaces and interfaces. They are full-potential all-electron methods and pseudopotential methods [10].

The first ones like FPLMTO [11] (full potential linearized muffin tin orbitals) and FLAPW (full potential linearized augmented plane wave) approaches display the advantage to be unified methods in that they can easily treat not only simple metals and semiconductors but also transition metals. They have computational advantages when systems are closely packed. However forces are difficult to be calculated and generally the energy is minimized with respect to atomic positions by hand. Therefore using pseudopotential methods seems to be more promising since these methods enable the forces to be calculated. In this case each atom of the studied structure is relaxed to its equilibrium configuration at which the computed forces on it are zero. In the pseudo-

potential approaches, the norm-conserving concept plays a central role in constructing modern pseudopotentials [5]. With the help of the Friedel sum rule, it can be shown that the norm-conserving requirement assures the highly desirable transferability, at the same time it imposes a quite rigid constraint on the pseudo-wave functions. Consequently, the basis size will be very large if the wave functions are expanded in plane waves. Thus the study of large systems, e.g. solid surfaces or interfaces modeled by a slab supercell, can become almost impossible computationally. The so-called ultra-soft pseudopotentials [12] were recently proposed to reconcile these conflicting aspects: accuracy, transferability, and plane-wave convergence. An other improvement of the method is to use a finite-temperature density functional approximation to solve the generalized Kohn-Sham equations via an efficient iterative matrix diagonalization scheme based on a conjugate gradient technique [13]. Within this framework, the free energy is the variational functional and a fractional occupation of the eigenstates is allowed which avoids the instability coming from the level crossing and quasidegeneracies in the vicinity of the Fermi level in metallic systems. It is an important point in the study of the ceramic-metal interfaces. Forces are then calculated through the Hellmann-Feynman theorem as the variational derivatives of the free energy with respect to the atomic positions. Since an analytical calculation of forces and the stresses is available, a geometry optimization can be readily carried out by using again the conjugate gradient method.

As seen in equation (1), the LDA (local density approximation) reduces the many-electron problem to the problem of one electron moving quantum-mechanically in the electrostatic potential from the nuclei and the electron density, plus an effective exchange-correlation potential derived from the density. Experience of the last fifteen years show that the most serious shortcomings of the LDA are seen in the binding which is usually too strong. Attempts to improve the LDA by adding lowest-order corrections in the gradient of the electron density has been proposed by a number of authors [14,15]. These generalized-gradient corrections (GGC's) have been tested in calculations of the total energies of atoms, molecules and solids. The GGC's improve the energetics of s,p-bonded metals and semiconductors with respect to the LDA as well as the energetics of the transition metals [16]. For an accurate description of the bonding at the ceramic-metal interface, we believe that such corrections are important.

## RESULTS AND DISCUSSION

We discuss here two series of *ab initio* based results which seem to be the more representative ones in the field of the metal-ceramic interfaces. The first example concerns the transition metal-oxide interface and the second one is dealing with the transition metal/SiC interface.

The Ag/MgO and Ti/MgO were the first metal-oxide interfaces calculated by using LDA-based linearized methods [17]. The Ag(100)/MgO (100) has received more attention because it has been also studied by high resolution microscopy [18]. The properties of metallic transition metals (TM) are often related to the filling of the d-band of electrons and it was the purpose of these authors to study the electronic properties of the metal-ceramic interfaces as a function of the filling of the d-band. Ag is characterized by having a filled d-band while Ti has a partially filled d-band. Both

metals display similar atomic volumes and therefore leads to an interface with a similar weak misfit in the lattice parameters. The unit cell for TM/MgO interface in (001) orientation contains three layers of MgO in contact with three (100) layers of transition metal. The oxide layers parallel to the interface are stoichiometric and therefore charge neutral. Three possible adsorption sites of TM atoms on the MgO (100) surface, i.e. above the O atom, above the Mg atom, or in the hollow site, are considered in these calculations. From the sets of total-energies calculations, the stablest configuration is found to be TM on O, followed by the hollow site and then the TM on Mg position. This agrees well with an other *ab initio* calculation [19] and with two other *ab initio* calculations but performed for a monolayer of TM on MgO [20,21]. However the work of separation does not agree so well as seen in table I.

Table I.  
Calculated work of separation for Ag/(100)MgO,  $\text{Jm}^{-2}$  for the three adsorption sites. The first two results are for a monolayer of Ag.

Mg	O	hollow	Reference
0.63	0.81	0.74	HF [21]
	0.54		LDA [20]
0.54	0.95		LDA [19]
0.7	1.6	1.1	LDA [17]
	0.45		experiment [18]

The difference between the results obtained for the monolayer of TM and the multilayer of TM is not too surprising since the electronic structure and the relaxation process are very different in both cases. Let us mention that this effect has been carefully studied in the case of the niobium-sapphire interface where a fully atomic relaxation has been performed by using the very efficient pseudopotential approach [22]. Two series of calculations have been performed, one with a monolayer of Nb in contact with O-terminated  $\text{Al}_2\text{O}_3$  (0001) surface, and the other with eight layers of Nb also in contact with the same surface. For the latter case the metal shows appreciable interlayer relaxation near the interface. For instance the Nb at the interface is 1.14 Å from the O plane, compared to 0.96 Å in the monolayer and 0.84 Å unrelaxed. At the same time, the second plane of Nb has relaxed towards the interface, so that the spacing between the first and second layers of Nb at the interface is reduced from 0.95 Å (bulk value) to 0.55 Å. The lattice propagation has also visibly propagated to the middle of the Nb slab. Such different behaviors have strong consequences on the work of separation. Indeed the true geometry of the metal-ceramic interface has to be considered avoiding geometrical approximations introduced by the computational methods. It is also the reason why the results provided by the cluster approaches have to be regarded circumspectly.

On the other hand, the Hartree Fock (HF) and the LDA methods for the monolayer differ by over 30% and even the two LDA methods for the multilayer differ by about 15%. In the future, it will be necessary to investigate and to reduce this level of uncertainty.

Turning to the Ti/MgO calculations, the procedure was the same as for Ag/MgO. However, in this case, the work of separation is somewhat larger, 2.2  $\text{Jm}^{-2}$ . A careful

analysis of the electronic structure at the interface shows clear signs of hybridization of the d-band of Ti with the O-2p band. The Fermi level is still about the same distance above the valence band in MgO, as seen for Ag, but there are now unoccupied antibonding states from the d-p hybridization and we expect the adhesion to be stronger than for Ag it is. These results show that a significant covalent/metallic contribution is evidenced by the role played by the filling of the d-band. However a substantial ionic component to the adhesive bond is also revealed in the electron density plots for both systems [7]. For instance, in the case of Ag/MgO interface, there is a charge redistribution of exactly the type one would expect from the image theory [23,24], namely a depletion of electrons on the metal adjacent to O and a piling up of electrons on the metal atoms adjacent to Mg. Then to conclude this first part, let us recall that the power of the first principles studies is their ability to provide insights into bonding mechanisms, gained from density of electronic states and electronic density distributions. There are no *ab initio* calculations for metal-ceramic interfaces in which the ceramic is not an oxide. Silicon carbide is an high-strength, high-temperature semiconductor ceramic material which has potential applications in high-temperature electronic devices. From a more fundamental point of view, SiC is an extremely intriguing group-IV semiconductor since many of its properties can be expected to be related to those of diamond and silicon in interesting way. While these elemental semiconductors exhibit only one stable phase at room temperature, the compound semiconductor SiC exists in very many polytypes and exhibits a relatively large ionicity. The silicon carbide surfaces display also a large variety of structures and compositions. SiC surfaces may be non polar or polar (in this case, Si- or C-terminated), they can adopt more or less complicated reconstruction geometries, depending on the polytype. Therefore it seems to be very interesting to explore the binding, adhesion, and nature of bonding between all these possible surfaces and metals.

From an experimental point of view, the adhesive properties of the liquid metal/SiC interfaces have been recently studied by Rado [25]. Among an important series of results, the author shows that the transition metal/SiC interface is very reactive but this reactivity can be controlled by adding silicon in the liquid metal. This reactivity is due to the strong interaction between silicon and transition metals at the interface, leading to the occurrence of silicide compounds. A nice correlation has been made between the work of immersion and the interaction parameter  $\lambda_{\text{Me-Si}}$  as derived in the Miedema's formulation [26]. Finally the geometry of the SiC surface does not seem to play a major role. Therefore it seems important to identify the nature of the transition metal/SiC adhesion bond.

We present preliminary results by studying the transition metal (TM)/ $\beta$ SiC(111) interface. Using the supercell technique, we employ eight layers of SiC and eight layers of TM. The lower four atomic layers of SiC are fixed in the bulk configuration. We optimize the structure by calculating the forces using the ultra soft-pseudopotentials [27]. We move the atoms of the upper four SiC layers and the TM atoms. The Si-terminated surface of  $\beta$ SiC is more particularly examined and for TM elements, we choose Ti, Fe and Ni. With this choice, we hope to emphasize the effects of the d-band filling on the adhesive properties of the TM/ $\beta$ SiC interface. The calculated work of separation of the three interfaces are 3.10, 1.75 and 4.65 Jm<sup>-2</sup> for Ni, Fe and Ti, respectively. Let us mention that our result for the work of separation of Ni/ $\beta$ SiC interface is in excellent agreement with

the one obtained by Rado, namely  $3.1 \pm 0.2 \text{ Jm}^{-2}$ . The parabolic behavior of the work of separation as a function of the d-band filling of the transition metal can be understood from the electronic structure of the TM/ $\beta$ SiC interface.

The first point is that this evolution of the work of separation as a function of the d-band filling of the transition metal is very similar to the one observed for bulk compounds. Indeed the heats of formation are -46, -39 and -79 kJ/atom for NiSi, FeSi and TiSi respectively [26]. For bulk compounds, Pasturel et al. [28] have provided a covalent scheme of the electronic structure of these compounds to explain this peculiar behavior. The densities of states (DOS) of the bulk TMSi alloys are characterized by a strong mixing of the d states of TM with the sp states of Si and the occurrence of a pseudogap at the top of the d-band. The peak located just below this pseudogap is due to the very weakly coupled d-states while the strong d-sp mixing is characterized by the lower energy peak and by the group of states which lie above the pseudogap. Such a mixing gives an alloy density of states which is very dissimilar to that in pure metals and this analysis indicates that the bonding in these systems is rather covalent than ionic.

This peculiar effect allows to determine the qualitative features of the heat of formation along a d series: there are two main contributions.

The first effect is this hybridization between the d-band of TM and the s and p bands of silicon which leads to sp-d bonding and antibonding hybrids, and to nonbonding d states as explained above. As is the case for the bonding energy of a diatomic molecule, filling bonding orbitals increases the bond strength, filling nonbonding orbitals has little effect, and filling antibonding orbitals reduces the bond strength. This hybridization leads to a term in the heat of formation for compound of a fixed sp element with the transition metals that becomes more bonding as the bonding hybrids are filled, remains flat as the nonbonding states are filled, and becomes rapidly less bonding as the antibonding states are filled. Since Ti has four electrons in its valence shell as does silicon, TiSi has eight electrons per unit cell which fills the eight bonding states given by the band-structure calculations [29]. It is constant during the filling of the nonbonding states up to FeSi with 12 electrons per unit cell, then it decreases as the antibonding states are filled.

By inserting the sp element into the transition metal lattice, the d-band is narrowed and thus the d-band-broadening contribution to the cohesive energy, which dominates the transition-metal cohesive energy, is reduced: this is the second effect. The loss of the d-bond energy is roughly proportional to the volume of the non-transition-metal constituent and to the strength of the d-bonding in the transition-metal constituent. Therefore, when considering compounds with a fixed element like Si, the loss varies parabolically across the transition-metal row with its maximum near the center of the row. The heat of formation is the sum of these two schematic components. The fact that the heats of formation from TiSi to NiSi alloys display a parabolic behavior shows that the expansion energy is the main factor to explain this evolution.

The close correspondence between the evolution of the heat of formation and the work of adhesion along this series indicates that the interface is reactive with the formation of a TMSi alloy. Using these arguments we can suggest some possibilities to diminish the reactivity of the (TM)/ $\beta$ SiC(111) interface. (i) modifying the electronic

concentration to have less filled bonding states or to have more filled antibonding states. For instance CuSi alloy with 15 electrons fills more antibonding states than NiSi alloy and consequently its heat of formation and its work of separation will be smaller. It is also possible to play with the contribution due to the expansion energy. For instance 4d and 5d TM display cohesive energies which are larger than the cohesive energies of the 3d TM and therefore we can predict a decrease of the adhesive properties of the 4d(or 5d)TM/ $\beta$ SiC(111) due to an increase of the expansion-energy contribution.

## CONCLUSIONS

We have given a short overview of the state of the art of *ab initio* calculations of adhesive properties at metal-ceramic interfaces. The main results can be summarized as follows.

- (i) The number of atomic layers in the slab has to be sufficient in order to recover bulk properties for both materials which form the interface. The knowledge of the atomic positions at the interface is also essential. Among the different techniques, the pseudopotential method is likely to be increasingly applied to these systems since it is the first approach which enables a full relaxation of the atoms.
- (ii) A degree of self-consistency, such as included in the LDA calculations, is necessary for obtaining a reliable electronic structure, since it determines the position of the Fermi level in the density of states.
- (iii) One of the most advantages of the *ab initio* studies is their ability to provide insights into bonding mechanisms, gained from density of electronic states and electron density distributions.

At this stage further work is necessary to establish the quantitative reliability of the *ab initio* methods for the work of separation of metal-ceramic interfaces although our results for TM/ $\beta$ SiC are very encouraging. Moreover we think that the *ab initio* study of the chemistry of segregation of interfaces is possible using the same techniques employed to study the chemistry segregation of surfaces [29]. These approaches can also open the way to develop simpler, semi-empirical models of the chemical bonding. Such models will be an invaluable help to study more quantitatively the role of misfit dislocations on the work of separation.

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