Ab-initio study of metal-zirconia interfaces

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Ab-initio study of metal-zirconia interfaces

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Abstract. A comparative theoretical study of metal-zirconia interfaces with BCC and FCC
metals was performed using pseudopotential approach with LDA and GGA approximation for
exchange-correlation functional. It was shown that the high adhesion can be achieved at the O-
terminated Me/ZrO2(001) interface with BCC metals that is related to large charge transfer
from metal film to substrate and increase of an ionic contribution in the chemical bonding. The
structural and electronic factors which are responsible for decrease of adhesion at differently
oriented metal-zirconia interfaces are discussed. The influence of CaO, MgO and Y2O3 doping
on the work of separation (Wsep) at Me(001)/c-ZrO2(001) is analyzed.

1. Introduction
Phenomena occurring at metal–ceramic interfaces are very important in many technological processes
and applications. The functional properties of corrosion-resistant coatings, high temperature
composites and electronic materials depend strongly on the adhesion at the metal–ceramic interface
[1]. Layered composite materials consisting of magnetic metal foils and insulating oxide layers can be
used for the cores of motors, generators, transformers, etc. [2]. There are several reviews concerning
the relationship between chemical bonding at the metal/ceramic interfaces and mechanical properties
of materials [3,4]. In most studies the metal-alumina interfaces were considered [5-8]. Less attention
was paid to metal-zirconia (Me/ZrO2) interfaces. Ab-initio methods within the density functional
theory (DFT) were applied to study the electronic structure of metal–ceramic interfaces in order to
understand metal-ceramic cohesion at the microscopic level. In most papers concerning metal-zirconia
interfaces the bonding at the Ni/ZrO2 interface was discussed in detail [9-11]. In [9] authors predicted
very strong adhesion at the Ni/ZrO2(111) interface due to the formation of localized interface bonds.
The existence of strong chemical bonding at the Ni(100)/ZrO2(100) interfaces was also demonstrated
in the work of Beltran et al. [10]. Two different types of interactions can provide this strong interfacial
stronger interaction at the Ni/(ZrO2)O(001) interface was shown for the less stable configuration (with
a Ni interfacial atom located in the next-Zr or Zr2 (figure 1) position than that considered in [10] (Ni
in the O-bridge position). It is necessary to point out that generalized gradient approximation (GGA)
was used in [10] whereas we applied local density approximation (LDA) in [11]. Both obtained results

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are in disagreement with experiments which suggest a weak interaction between Ni films and zirconia \[12,13\]. This discrepancy between theoretical and experimental results can be attributed to the presence of surface vacancies. It should be noted that the cubic phase of zirconia exists above 2370 °C \[14\]. It can be stabilized at lower temperatures by addition of other oxides (Y\(_2\)O\(_3\), MgO, CaO, etc.), which leads to the appearance of oxygen vacancies. The appearance of metal impurities leads to a decrease of the electrostatic interaction and the presence of oxygen vacancies, especially near an interface, can provide lower adhesion \[1,15\]. The influence of Fe additions on adhesion was also considered in our work \[11\]. It was shown that in the case of Ni–Fe ordered alloys the adhesion depends strongly on the composition of the interfacial layers and their magnetic states. The adhesion at metal/zirconia interfaces was considered in details by Muçoz et al. in review \[1,16\].

\[\text{Figure 1. Atomic structure of the interfacial layers of } \text{Me}(001)/\text{ZrO}_2(001), \text{Me}(110)/\text{ZrO}_2(110) \text{ and } \text{Me}(111)/\text{ZrO}_2(111) \text{ interfaces. Atoms of } \text{Me} \text{ and } \text{Zr} \text{ are depicted by large grey and white circles and } \text{O} \text{ atoms are shown by small black circles.} \]

In this work we present the results of a comparative study of adhesion at Me/ZrO\(_2\) interfaces with BCC and FCC metals and examine the influence of alloying oxides (CaO, MgO, Y\(_2\)O\(_3\)) on the electronic bonding properties at the metal-zirconia interfaces.

2. Computational details

Atomic and electronic structure of the Me/ZrO\(_2\) interfaces were calculated using the pseudopotential approach with plane wave basis implemented in the Vienna ab-initio simulation package (VASP) \[17-19\]) and ultrasoft pseudopotentials \[20\]. Both LDA \[21\] and GGA-PBE \[22\] approximations for exchange-correlation functional were used. The equilibrium lattice parameter of cubic zirconia was found to be 5.082 Å using LDA which is in good agreement with the experimental value of 5.088 Å. The application of GGA-PBE resulted in 5.126 Å. An energy cutoff of 500 eV for plane wave basis set, and a \(8 \times 8 \times 1\) Monkhorst-Pack \(k\)-points mesh for integration over the Brillouin zone were used in calculations. The total energies were converged up to \(10^{-4}\) eV. Metal-zirconia interfaces were modeled using a supercell approach with periodic boundary conditions. A sandwich configuration of the interface with a zirconia slab between two metal slabs with a vacuum region not less than 8 Å between them was used. It is known that the (001) and (111) surfaces of cubic ZrO\(_2\) are characterized by alternating layers of O and Zr atoms and can be terminated by either Zr or O atomic planes whereas (110) surface has stoichiometric composition as bulk. In order to describe the cubic-ZrO\(_2\)(001) surface it is sufficient to use six atomic layers of O and five or seven atomic layers of Zr depending on surface termination. There are two different types of interfaces (Me-Zr and Me-O), depending on the termination of the (001) surface (either Zr or O atomic planes). One can see in figure 1 Me atoms are
twofold coordinated by O atoms in the case of the O-bridge position but they are fourfold coordinated by O atoms in the case of Zr₂ position at the Me-O interface. In the case of the Zr-terminated oxide surface Me atoms can occupy the next O atoms or O₂-position (figure 1). Five atomic layer metal films were considered at the Me/ZrO₂ interfaces. The atoms of the three central atomic layers in the oxide film were fixed with the spacing between the layers being equal to its value in the bulk. The atoms of other layers including those in metal films were relaxed until the forces acting on the atoms were less than 0.025 eV/Å. Considered geometries for the case of (110) and (111) interfaces are shown in figure 1 as well.

The work of separation is a fundamental quantity, which controls the mechanical strength of the metal-ceramic interface. It is the work needed to separate the interface into two free surfaces and can be defined as

\[ W_{sep} = \frac{(E_{me} + E_{ox} - E_{me-ox})}{2S}, \]

where \( E_{me} \) is the total energy of supercell containing the multilayered slabs; \( E_{me} \) and \( E_{ox} \) are the total energies of the same supercell containing a single slab of the metal or oxide, respectively; \( S \) is the interface area and the factor 2 takes into account the presence of the two equivalent interfaces within a unit cell.

3. Results and discussion

The calculations of \( W_{sep} \) at the O-terminated \( Me(001)/ZrO_{2}(001) \) interfaces with FCC metals (\( Me=Fe, Ni, Cu, Rh, Pd, Pt, \) etc.) with respect to the Me-O cleavage plane indicate much stronger chemical bonding at the interface with the metal in the O-bridge position than with the metal in the Zr₂-position. Weaker adhesion of the \( Me \) films to zirconia in this position is in accordance with equilibrium \( Me–O \) bond length which is slightly longer in the former case. The bonding mechanism is primary ionic interaction between \( Me \) and O atoms as can be clearly seen in figure 2 where the charge-density difference for Cu/ZrO₂ is presented.

Figure 2. Total charge density and difference \( \Delta\rho(\vec{r}) = \rho_{me}(\vec{r}) + \rho_{ox}(\vec{r}) - \rho_{me-ox}(\vec{r}) \) (in the middle) at the Cu/ZrO₂(001) interface: Cu/(ZrO₂)₀⁻ (left) and Cu/(ZrO₂)Ｚr (right).

One can see the charge depletion region near Cu atoms and the corresponding charge accumulation region near O atoms. The charge-density distributions indicate that the Zr- and O-terminated interfaces differ in terms of the mechanism of bonding. Figure 2 reveals a metal bonding character between \( Me \) and Zr atoms at the \( Me-Zr \) interface, which arises from \( s-d \) and \( d-d \) hybridizations. Charge redistribution leads to the polarization of \( Me \) atoms (especially Ni, Fe atoms), therefore, the chemical bonding at the Zr-terminated interface is a combination of both metallic interaction and electron polarization. The estimation of the work of separation for example in the case of the Cu/ZrO₂(001)₀⁻ interface (table 1) corresponds to a rather strong bonding than that calculated in [10].
As can be seen from table 1 the scatter in the values of $W_{\text{sep}}$ at the Zr-terminated interfaces is less than 0.5 J/m$^2$ but it is larger at the O-terminated interface. Similar trends were obtained for other considered metals with FCC structure. Moreover the conclusions obtained for Cu are valid in the case of the HfO$_2$(001) substrate (table 1). For the Ni(001)/HfO$_2$(001) interfaces the values of $W_{\text{sep}}$ are equal to 5.85 and 7.45 J/m$^2$ for Hf- and O-terminated interface respectively, but these values are 5.13 and 7.35 J/m$^2$ for Zr- and O-terminations. Our calculations show that the usage of a nonlocal correction in the exchange-correlation functional in the form [22] leads to lower values of $W_{\text{sep}}$ (table 1). The difference in $W_{\text{sep}}$ is significant less at the Zr-terminated interface due to more effective screening of Zr-states in oxide.

Table 1. Work of separation at Cu-zirconia interfaces with respect to their termination, configuration of the metal film as well as approximation for the exchange correlation potential ($V_{\text{xc}}$).

<table>
<thead>
<tr>
<th>Interfaces</th>
<th>$V_{\text{xc}}$</th>
<th>Configuration$^a$</th>
<th>$W_{\text{sep}}$ (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(001)/ZrO$<em>2$(001)$</em>{Zr}$</td>
<td>LDA</td>
<td>Zr1</td>
<td>3.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O2</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O-bridge</td>
<td>3.69</td>
</tr>
<tr>
<td>Cu(001)/ZrO$<em>2$(001)$</em>{Zr}$</td>
<td>GGA</td>
<td>O2</td>
<td>3.25 (3.66 [16])</td>
</tr>
<tr>
<td>Cu(001)/ZrO$_2$(001)$_O$</td>
<td>LDA</td>
<td>O-bridge</td>
<td>6.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O1</td>
<td>5.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zr2</td>
<td>5.84</td>
</tr>
<tr>
<td>Cu(001)/HfO$<em>2$(001)$</em>{Zr}$</td>
<td>GGA</td>
<td>O-bridge</td>
<td>4.90 (5.08 [16])</td>
</tr>
<tr>
<td>Cu(001)/HfO$_2$(001)$_O$</td>
<td>LDA</td>
<td>O2</td>
<td>4.07</td>
</tr>
<tr>
<td>Cu(110)/ZrO$_2$(110)</td>
<td>LDA</td>
<td>O1</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zr1</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zr2</td>
<td>1.50</td>
</tr>
<tr>
<td>Cu(111)/ZrO$_2$(111)$_O$</td>
<td>LDA</td>
<td></td>
<td>0.65</td>
</tr>
<tr>
<td>Cu(111)/ZrO$<em>2$(111)$</em>{Zr}$</td>
<td>LDA</td>
<td></td>
<td>3.70</td>
</tr>
</tbody>
</table>

$^a$ Symbols Zr1, O1, etc. denote interfacial atoms of oxide above which the metal atoms are located.

The investigation of the influence of the metal electronic structure on the adhesion at the Me(001)/ZrO$_2$(001)$_0$ interface shows that the work of separation decreases in the row of isoelectronic metals (5.96 J/m$^2$ (Ni 3$d^8$4$s^3$), 3.53 J/m$^2$ (Pd 4$d^{10}$5$s^5$) and 3.26 J/m$^2$ (Pt 5$d^{10}$6$s^5$), here GGA-PBE results are presented) due to filling of the $d$-band and decrease of charge transfer from the metal to the substrate. The structural factors caused by the increase of the metal and oxide lattices mismatch at the interface (2.06%, 9.11% and 9.74% for Ni, Pd and Pt, respectively) influence the work of separation also. It should be noted that for metal with not fully occupied $d$-band (Rh(001)/ZrO$_2$(001)$_0$) the value of the $W_{\text{sep}}$ is still high (5.17 J/m$^2$) which is due to an increase of ionic contribution in the chemical bonding. The used projected augmented wave method (PAW-LDA) or PP LDA results in an even higher value of $W_{\text{sep}}$ (6.72 J/m$^2$) than obtained with the pseudopotential GGA-PBE approach. The work of separation in the case of Pd film is 4.99 J/m$^2$ (PAW-LDA) and 5.04 J/m$^2$ (PP-LDA). The calculated values of $W_{\text{sep}}$ in the case of Pt(111) and Pt(001) films are 3.37 J/m$^2$ and 3.26 J/m$^2$, respectively. In the case of Pt film $W_{\text{sep}}$ depends slightly on the film orientation. It should be noted that adhesion of Cu in the case of non-polar stoichiometric ZrO$_2$(110) surface is significant less pronounced than at the interfaces with polar non stoichiometric Zr-terminated surfaces (001) or (111). The lower values of $W_{\text{sep}}$ were obtained in the case of Me configuration in Zr1 i.e. above Zr of the first interfacial layer. Low $W_{\text{sep}}$ (0.63 J/m$^2$) at the Cu/ZrO$_2$(111)$_O$ interface in comparison with that for (001) interfaces can be explained by the following factors: decrease of charge transfer to oxygen, increase of interfacial distance and decrease of Me-O bonds. Note that three from four oxygen atoms at the (111) interface are located in the position which is twofold coordinated by metals whereas the fourth atom is located in the Me-top position. Some metal atoms form the bond with Zr of the second
layer from interface (bond lengths are varied from 2.50 up to 2.86 Å) whereas all metal atoms are bonded to oxygen atoms of interfacial layer in the case of (001).

At the Ni(111)/ZrO$_2$(111) interface the $W_{\text{sep}}$ reaches up to 1.45 J/m$^2$ due to an increase of the charge transfer. Electronegative oxygen can much easier get electrons for filling its $p$-band from Ni since its $d$-band is not fully occupied as that from Cu. Spin-polarized calculations of differently oriented Ni-zirconia interfaces demonstrate the decrease of $W_{\text{sep}}$ by $\sim$0.05-0.3 J/m$^2$ and an increase of the interfacial distance of 0.05-0.1 Å in dependence of the orientation and termination interface if the magnetism of Ni is taken into account. Note that the adhesion of the metal monolayer is higher than that for the metal film. The increase of $W_{\text{sep}}$ up to 1.65 J/m$^2$ in the case of a Ni-monolayer correlates with the decrease of interfacial distance from 1.66 Å up to 1.55 Å. In general, our calculations demonstrate that high values of adhesion energy can be achieved at the metal-zirconia interface with BCC metals such as Nb, Ta, Mo, W (table 2) in the case of $\text{Me-Al}_2\text{O}_3$(0001). The chemical interaction at the interface is mainly ionic (figure 3) with large charge transfer ($\sim$ 0.25-0.30 el) from the metal film to each oxygen atom.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Method</th>
<th>$W_{\text{sep}}$(J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb(001)/ZrO$_2$(001)$_O$</td>
<td>PAW-LDA</td>
<td>10.26 (10.29)</td>
</tr>
<tr>
<td></td>
<td>PAW-PBE</td>
<td>8.82</td>
</tr>
<tr>
<td>Ta(001)/ZrO$_2$(001)$_O$</td>
<td>PAW-LDA</td>
<td>10.68</td>
</tr>
<tr>
<td></td>
<td>PAW-PBE</td>
<td>9.30</td>
</tr>
<tr>
<td>Mo(001)/ZrO$_2$(001)$_O$</td>
<td>PAW-LDA</td>
<td>9.80 (9.94)</td>
</tr>
<tr>
<td></td>
<td>PAW-PBE</td>
<td>9.65</td>
</tr>
<tr>
<td>W(001)/ZrO$_2$(001)$_O$</td>
<td>PAW-LDA</td>
<td>(10.03)</td>
</tr>
<tr>
<td></td>
<td>PAW-PBE</td>
<td>9.35</td>
</tr>
</tbody>
</table>

In order to study the influence of alloying oxide CaO, MgO and Y$_2$O$_3$ on the work of separation at the Cu/ZrO$_2$(001) interface we increased the size of computational cell. This allows us to decrease the concentration of defects. The positions of substitution impurities and oxygen vacancies are shown in figure 4. An O-vacancy was introduced removing one out four O atoms.

**Figure 3.** Charge density difference $\Delta \rho$ at Mo/ZrO$_2$(001)$_O$ (left) and W/ZrO$_2$(001)$_O$ (right) interfaces.

**Figure 4.** Atomic structure of the Cu/ZrO$_2$(001) interface with alloying oxide CaO (MgO) or Y$_2$O$_3$ at O-terminated (left) and Zr-terminated (right) interfaces.
Table 3. Work of separation (in J/m$^2$) at ideal and defective Cu/ZrO$_2$(001) interface

<table>
<thead>
<tr>
<th>Interface</th>
<th>Ideal</th>
<th>O-vac</th>
<th>CaO</th>
<th>MgO</th>
<th>Y$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/ZrO$<em>2$(001)$</em>{Zr}$</td>
<td>3.25</td>
<td>3.03</td>
<td>2.26</td>
<td>2.44</td>
<td>2.64</td>
</tr>
<tr>
<td>Cu/ZrO$<em>2$(001)$</em>{O}$</td>
<td>4.90</td>
<td>2.96</td>
<td>2.98</td>
<td>2.93</td>
<td>4.63</td>
</tr>
</tbody>
</table>

As can be seen from table 3 the adhesion energy is reduced significantly on both interfaces in the case of CaO alloying. Appearance of Ca or Mg at the Zr-sites leads to a decrease of the hybridization of Me-Zr states which provides more substantial lowering of adhesion at the Zr-terminated interface than in the case of Y substitution impurity.

In the O-terminated interface the effect of the O-vacancies on the adhesion is pronounced more significantly and can even lead to instability of the cubic lattice and its transformation into the monoclinic one. The decrease of $W_{\text{sep}}$ at the O-terminated interface is caused by the reduced number of interfacial bonds induced by the O-vacancies [11]. Substitution impurities stabilize the cubic structure due to keeping bond strengths as it was shown in [1]. The estimation of interatomic bonds and interfacial distances were performed in the presence of both defects (O-vacancy and Me-impurity). In the case of YSZ the restore of interatomic bonding occurs which decreases the critical influence of the O-vacancies on $W_{\text{sep}}$.

4. Conclusion
A systematic investigation of the adhesion properties at metal-zirconia interfaces with FCC and BCC metals has been performed by $ab$-initio density functional theory methods. General trends in the change of $W_{\text{sep}}$ with respect to structure, composition of interfacial layers, and electronic structure of metal as well as defects are established. High adhesion is found for BCC transition metals at the O-terminated zirconia polar (001) surface that can be connected with their partially occupied $d$-band and a larger ionic contribution to the chemical bonding in comparison with FCC metals. It was shown that in zirconia stabilized by other oxides as CaO, MgO, Y$_2$O$_3$ critical influence of the O-vacancies in the interfacial oxide layers on $W_{\text{sep}}$ can be partly compensated by substitutional impurities which lead to large rearrangements of the O and Zr atoms and restoration of the interfacial distance.

References