Interaction of oxygen with ZrC(001) and VC(001): Photoemission and first-principles studies

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High-resolution photoemission and first-principles density-functional calculations were used to study the interaction of oxygen with ZrC(001) and VC(001) surfaces. Atomic oxygen is present on the carbide substrates after small doses of O₂ at room temperature. At 500 K, the oxidation of the surfaces is fast and clear features for ZrO_x or VO_x are seen in the O(1s), Zr(3d), and V(2p_{3/2}) core levels spectra, with an increase in the metal/carbon ratio of the samples. A big positive shift (1.3–1.6 eV) was detected for the C 1s core level in O/ZrC(001), indicating the existence of strong O↔C or C↔C interactions. A phenomenon corroborated by the results of first-principles calculations, which show a CZrZr hollow as the most stable site for the adsorption of O. Furthermore, the calculations also show that a C↔O exchange is exothermic on ZrC(001), and the displaced C atoms bond to CZrZr sites. In the O/ZrC(001) interface, the surface C atoms play a major role in determining the behavior of the system. In contrast, the adsorption of oxygen induces very minor changes in the C(1s) spectrum of VC(001). The O↔V interactions are stronger than the O↔Zr interactions, and O↔C interactions do not play a dominant role in the O/VC(001) interface. In this system, C↔O exchange is endothermic. VC(001) has a larger density of metal *d* states near the Fermi level than ZrC(001), but the rate of oxidation of VC(001) is slower. Therefore the O/ZrC(001) and O/VC(001) systems illustrate two different types of pathways for the oxidation of carbide surfaces.

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I. INTRODUCTION

The early transition metals have a low cost and their compounds play a very important role in many areas of physics, chemistry, and materials science.^{1–8} Traditionally, the oxides have been the compounds with the largest number of technological applications,^{1,3,5,9–12} but in the last two decades carbides and nitrides are receiving a lot of attention.^{6–8,13–25} In broad terms, early transition metal carbides display a unique combination of the physical properties characteristic of noble metals and ceramics.^{6,7,25} Many early transition metal carbides are good electrical and thermal conductors while possessing ultrahardness and very high melting points.^{6,7} Furthermore, some of them are able to catalyze the transformation of hydrocarbons,^{8,26} the conversion of methane to synthesis gas,^{27,28} and desulfurization reactions.^{8,23,29}

Typically, early transition metals are very reactive, are not stable under chemical environments containing light elements, and exhibit a tendency to form compounds (oxides, nitrides, sulfides, carbides, phosphides). The inclusion of C into the lattice of an early transition metal produces a substantial gain in stability and moderates the chemical reactivity of the system.¹⁴ Usually, the formation of metal-carbon bonds modifies the electronic properties of the metal, producing a decrease in its density of states near the Fermi level and a metal→carbon charge transfer.^{8,14,15,18,25} In these materials, the chemical bonding exhibits a mixed character.^{25,30–33} For example, the valence bands of VC show

a strong hybridization of the V(3d) and C(2p) states as expected for a covalent compound,^{25,31} but there is, nevertheless, a rather large degree of ionicity in the V–C bonds with a positive Mulliken charge of $\sim 1e$ on the V atoms.²⁵ Among the carbides, the magnitude of the metal→carbon charge transfer increases following the VC<TiC<ZrC<TaC sequence, and there can be large variations in the relative density of the C(2p) and metal *nd* states near the Fermi level.²⁵ These differences in the electronic properties can affect the chemical reactivity of these compounds.

The interaction of oxygen with surfaces of metal carbides is an important issue. The catalytic properties of metal-carbides can be drastically modified by adsorption of oxygen from the air or by reaction with O centers of oxide supports.^{8,26–29} In addition, oxygen also affects the performance of metal-carbide coatings used in the fabrication of mechanical and electronic devices.^{6,7,21,22} The generation of an oxide film on top of the carbide can lead to a degradation of the conductivity and hardness of the system,^{6,7} and oxo-carbides can have interesting physical properties on their own.^{7,8,22} Several experimental studies have investigated the interaction of oxygen with well-defined surfaces of metal carbides,^{21,22,34–36} but the microscopic or atomic details of the oxidation process are not fully understood. A key point is the relative importance of the oxygen↔metal and oxygen↔carbon interactions.^{21,22,36} Usually, it is assumed that the C sites of a metal carbide surface play a secondary or minor role in the chemical properties of the system.^{5,8,18}

However, recent photoemission studies for O/TiC(001) point to the existence of strong oxygen $\leftrightarrow$ carbon interactions.^{21,36} A phenomenon corroborated by the results of first-principles density-functional (DF) calculations, which predict a CTiTi hollow as the most stable site for the adsorption of O.³⁶ In contrast, data of high-resolution electron energy loss spectroscopy (HREELS) for O/VC(001) show the presence of V–O bonds and negligible oxygen $\leftrightarrow$ carbon interactions.²¹ The differences in the behavior of the O/TiC(001) and O/VC(001) systems could be a consequence of variations in the electronic properties of the metal carbides.^{21,25} In particular, one may wonder whether among the TM carbides, the behavior of O/TiC(001) is atypical or, on the contrary, it is to be expected. In this work, we use high-resolution photoemission and first-principles DF calculations to study the adsorption and reaction of oxygen with ZrC(001) and VC(001) surfaces. ZrC and VC are among the most extensively studied transition metal carbides.^{7,8,21,25,31} They adopt a cubic NaCl lattice,^{7,37} as TiC, and their (001) face contains the same number of metal and C atoms.

This paper is organized as follows. Section II gives a description of the technical details of the work, including the experimental and theoretical methods used. Section III presents synchrotron-based high-resolution photoemission spectra for a series of O/ZrC(001) and O/VC(001) systems, examining the effects of O adsorption on the carbon and metal surface atoms. In Sec. IV, density-functional calculations are used to examine the nature of the O–ZrC and O–VC bonds, and the energetics for the dissociation of O₂ and oxidation of the carbide surfaces is described in Sec. V. Finally, Sec. VI summarizes the main conclusions of the present work.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Photoemission and XPS experiments

The photoemission studies for the adsorption of oxygen on ZrC(001) and VC(001) were performed at the U7A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). This beamline is equipped with a conventional ultrahigh-vacuum (UHV) chamber (base pressure $\sim 5 \times 10^{-10}$ Torr) that contains a hemispherical electron energy analyzer with multichannel detection, instrumentation for low-energy electron diffraction (LEED), a quadrupole mass spectrometer, and a dual anode Mg/Al $K\alpha$ x-ray source.^{13,36} The photoemission spectra reported in Sec. III were recorded using photon energies of 380 eV for the Zr(3*d*) and C(1*s*) core levels or 625 eV for the O(1*s*) and V(2*p*) ones.^{13,36,38} At these photon energies the excited electrons had kinetic energies in the range of 85–200 eV and, therefore, photoemission probed only the composition of the first 2 to 3 layers of the sample. The overall instrumental energy resolution in the photoemission experiments was ~ 0.3 eV. The binding energy scale in the photoemission spectra was calibrated by the position of the Fermi edge in the valence region. Additional experiments of XPS were carried out at the Tokyo Institute of Technology (TIT) using an UHV chamber (base pressure ~ 1

$\times 10^{-10}$ Torr) that has capabilities for this technique (Al $K\alpha$ x-ray source, hemispherical electron energy analyzer) plus LEED and Auger electron spectroscopy (AES).^{13,36}

The surfaces of the carbides were prepared at the TIT. Bulk crystals of ZrC and VC were aligned by x-ray diffraction, then cut to within 1° of the desired crystallographic plane. The produced surfaces were polished with diamond paste down to a grit size of $0.15 \mu\text{m}$. In the UHV chambers at BNL and the TIT, the ZrC(001) and VC(001) surfaces were mounted and cleaned following the methodology described in previous works.^{13,21,36} Surface impurities were removed by ion sputtering and the metal/carbon ratio was kept equal to one by exposing the sputtered surfaces to small amounts of C₂H₂ or C₂H₄ at 800–900 K. At these high temperatures the C from the hydrocarbons is incorporated into the lattice of the metal carbide and the hydrogen evolves into gas phase.⁸ The cleaning procedure led to a clear 1×1 diffraction pattern in LEED and no surface impurities in photoemission or XPS. The crystal growers estimated stoichiometries of ZrC_{0.96–0.99} and VC_{0.97–0.99} for the bulk samples, and, after cleaning, our quantitative XPS results showed surfaces with essentially a Zr/C or V/C ratio of one.^{21,39} For surfaces prepared in this way, images of scanning tunneling microscopy (STM) give a square crystal lattice with terraces that are $480\text{--}710 \text{ \AA}$ wide, separated by single and double step heights.³⁹

Molecular oxygen (99.995% purity) was dosed to the ZrC(001) and VC(001) surfaces at 300 or 500 K using dosing tubes with apertures located ~ 5 mm away from the sample. These dosing systems provided a large enhancement (>10 times) in the mass adsorbed with respect to dosing by backfilling the UHV chambers with O₂. The reported exposures of O₂ are based on the direct ion gauge readings without correction for the enhancement factors of the dosers.

B. First-principles density functional calculations

In this work, periodic DF calculations were performed using three different computational packages—CASTEP, VASP, and DMOL³—to take advantage of special features of these codes. The level of theory used here has been quite useful in previous studies that deal with the electronic properties and structure of carbide surfaces,^{25,36} the dissociation of O₂ on TiC(001),³⁶ and the bonding of small molecules to VC(001) and other carbide surfaces.^{13,23} With CASTEP,^{40,41} the valence electron densities were expanded in a plane wave basis set with k -vectors within a specified energy cutoff ($E_{\text{cut}}=400$ eV in our case).^{13,23,36} Tightly bound core electrons were represented by nonlocal ultrasoft pseudopotentials of the Vanderbilt type.⁴² In the calculations with VASP,⁴³ a plane-wave basis set was also used ($E_{\text{cut}}=415$ eV)²⁵ to expand the valence electronic states and the core electrons were represented by the projected augmented wave (PAW) method of Blöchl.⁴⁴ Within the DMOL³ code, the wave functions were expanded in a basis set of localized atomic orbitals.⁴⁵ In the DMOL³ calculations, *all* the electrons of C, O, Zr, and V were included and a numerical basis set of double- ζ plus polarization quality was used to describe the valence orbitals of each element.^{23,45} The all-electron calculations with DMOL³

(DF-AE in our notation) required more computer time than the pseudopotential calculations with CASTEP (DF-PSP in our notation) or the frozen-core calculations with VASP (DF-PAW in our notation). Thus, DMOL³ calculations were used only to examine key systems, while a systematic theoretical study was carried out with CASTEP and VASP. By working with CASTEP, VASP, and DMOL³, we were able to obtain a robust theoretical description for the O/ZrC(001) and O/VC(001) interfaces that was independent of the type of basis set used, of the approximation employed to treat the core electrons or the exchange-correlation potential used (see below).

Following previous works,^{13,23,25,36} we examined the bonding of O to the carbide surfaces using the generalized-gradient approximation (GGA) with the revised Perdew-Burke-Ernzerhof functional (RPBE),⁴⁶ CASTEP and DMOL³ calculations, or the so-called Perdew-Wang functional (PW91),⁴⁷ VASP calculations. Our main interest here is in bonding-energy variations when oxygen moves from one adsorption site to another on the ZrC(001) and VC(001) surfaces. DF calculations using the RPBE functional predicted an adsorption energy for CO on VC(001), 0.63 eV,²³ that is within 0.15 eV of the experimental value, 0.49 eV,⁴⁸ and gave a very good description of the bonding interactions of oxygen with TiC(001).³⁶ Nevertheless, even if one expects the RPBE functional to provide adsorption energies closer to experiment than those obtained by the PW91 method, it has also been pointed out that it tends to lead to worse results for bulk properties like lattice parameters and bulk moduli.⁴⁹ Also, there are examples where the RPBE functional may even overcorrect adsorption energies, thus predicting incorrectly binding strengths.⁵⁰ Therefore a comparison of results obtained using both PW91 and RPBE seems very convenient.

To model the ZrC(001) and VC(001) surfaces, we used the supercell approach^{40,41} with a vacuum of 12 Å between the slabs.^{13,23,25,36} In test calculations with CASTEP, the adsorption of one monolayer of O on ZrC(001) was investigated employing eight-, six-, and four-layer slabs, obtaining almost identical results independently of the slab thickness. The CASTEP and VASP results reported in Sec. IV are for six- and four-layer slabs, respectively. A four-layer slab was also used in the all-electron calculations with the DMOL³ code. The adsorbed oxygen was set only on one side of the slabs. The geometry of the adsorbate and of the first two slab layers were completely relaxed in the DF calculations. The O coverage values are here reported with respect to the number of metal ($M=\text{Zr}$ or V) atoms in the surface. Thus oxygen coverages of 1, 0.5, and 0.25 monolayer (ML) were modeled with the adlayer in $p(1\times 1)$, $p(2\times 1)$, and $p(2\times 2)$ arrays with respect to the lattice of Zr or V surface atoms. The adsorption energy of oxygen was defined as $E_{\text{ad}}=E_{\text{MC(001)}}+E_{\text{O}}-E_{\text{O/MC(001)}}$, where $E_{\text{O/MC(001)}}$, $E_{\text{MC(001)}}$ and E_{O} represent the total energies of the adsorbed system, the clean relaxed ZrC(001) or VC(001) surface, and that of a free O atom, respectively. Spin polarization was used for calculating atomic O or molecular O₂ in gas phase. After several tests, we found no need for spin polarization in calculations involving O/ZrC(001) and O/VC(001).

FIG. 1. Top panel: Variation of the intensity for the O(1s) signal for O/ZrC(001) and O/VC(001) as a function of the O₂ dose at 500 K. Bottom panel: Effects of oxygen adsorption on the Zr(3d)/C(1s) and V(2p_{3/2})/C(1s) intensity ratios. The dosing of molecular oxygen was done at 500 K and all the data were acquired with the same electron energy analyzer. Error bars are also indicated.

III. OXYGEN ADSORPTION AND OXIDATION OF ZrC(001) AND VC(001): PHOTOEMISSION AND XPS STUDIES

The top panel in Fig. 1 shows the uptake of oxygen for ZrC(001) and VC(001) at 500 K. The data indicate that ZrC(001) is somewhat more reactive than VC(001). A similar trend was found when the dosing of O₂ was done at 300 K. The variation of the metal/carbon ratio as a function of O₂ exposure at 500 K is shown in the bottom panel of Fig. 1. The reported values were calculated using the total areas under the corresponding Zr(3d), V(2p), and C(1s) photoemission features, and essentially reflect changes that occur in the first 2 to 3 layers of the samples (see Sec. II A). As the amount of adsorbed oxygen rises, there is an increase in the metal/carbon ratio that can be interpreted as a loss of carbon from the surface due to the formation of gaseous CO_x species and the generation of oxide films.^{21,36} Indeed, the photoemission results discussed below indicate that Zr–C or V–C bonds are being replaced by Zr–O or V–O bonds. We found that the loss of carbon was much larger at 500 K than at room temperature. Images of STM taken at the Tokyo Institute of Technology show that at room temperature the oxidation process is mainly localized at the step edges between

FIG. 2. O(1s) photoemission spectra for the dissociative adsorption of O₂ on ZrC(001) and VC(001) at 300 or 500 K. The spectra were curve fitted following the procedure described in Ref. 36. A photon energy of 625 eV was used to excite the electrons.

terraces of the surface.³⁹ In contrast, at 500 K, there is also a substantial oxidation of regions within the wide terraces of the ZrC(001) and VC(001) samples.³⁹ From the data in Fig. 1 we can conclude that the oxidation of ZrC(001) is faster than the oxidation of VC(001).

Figure 2 displays several O(1s) core-level spectra ($h\nu=625$ eV) taken after dosing molecular oxygen to ZrC(001) and VC(001) surfaces at room temperature and 500 K. The position observed for the O(1s) peak (531–528 eV) denotes the presence of atomic oxygen on/in the carbide surface/interface.^{21,36} In general, we found that at 300 or 500 K, O₂ adsorbs dissociatively on both ZrC(001) and VC(001) surfaces. In Fig. 2, there is a shift toward lower binding energy in the centroid of the O(1s) features as the dosing temperature increases. This is clear for ZrC(001) and less evident for VC(001). Curve fitting,⁵¹ after a simple background subtraction, indicates that there were at least two types of oxygen species in the carbide samples. In the O/ZrC(001) systems, the O(1s) peak located at ~ 528.8 eV is close to the position observed in our instrument for ZrO₂.³⁸ Thus one could have ZrO_x species on the surface [O(1s) features toward lower binding energy] together with O atoms chemisorbed on ZrC [O(1s) features toward higher binding energy]. This is because, according to simple charge transfer arguments, O(1s) features in oxidelike species shift toward lower binding energy, although it is important to realize that other mechanisms do also affect core level shifts.⁵² In the case of O/VC(001), the O(1s) features toward lower binding energy probably correspond to VO_x. This species has

FIG. 3. Zr(3d) and V(2p_{3/2}) photoemission spectra (b) for the adsorption of O₂ on ZrC(001) and VC(001) at 500 K. At the top of each panel are shown difference spectra, denoted as (b-a) and obtained after subtracting from (b) the normalized features (a) for clean ZrC(001) or VC(001) (Ref. 36). The electrons were excited using photon energies of 380 or 625 eV for the Zr(3d) and V(2p_{3/2}) levels, respectively.

been detected in HREELS experiments for O/VC(001).²¹ The relative intensity of the O(1s) peaks in Fig. 2 clearly corroborates that the oxidation of the carbides proceeds faster at elevated temperatures and it is easier to oxidize ZrC(001). Again, this is also less apparent for VC(001).

The Zr(3d) core-level spectra ($h\nu=380$ eV) acquired before and after dosing O₂ to ZrC(001) at 500 K are shown in the top panel of Fig. 3. The reaction with oxygen produced a line-shape change in the photoemission peaks and features appeared towards higher binding energy, consistent with the formation of ZrO_x species on the surface.³⁸ The peaks for ZrO_x become clearer in difference spectra. The Zr(3d_{5/2}) peak position never reached the value of 182.5 eV characteristic of pure ZrO₂,³⁸ even after dosing 100 L of O₂ at 500 K. The V(2p_{3/2}) core-level data ($h\nu=625$ eV) displayed in the bottom panel of Fig. 3 indicate the presence of VO_x in the O/VC(001) system. The new O-induced V(2p_{3/2}) features appear at 514.3 eV, well separated from the corresponding features of VC (513.1 eV), but not as deep in energy as the V(2p_{3/2}) peaks reported for VO₂ (515.8 eV) or V₂O₅ (517.0 eV).^{53,54}

Previous XPS studies indicate that the C(1s) core level of TiC(001) is affected by the oxygen adsorption.^{21,36} This phe-

FIG. 4. C(1s) photoemission data recorded after exposing ZrC(001) and VC(001) to O₂ at 500 K. A photon energy of 380 eV was used to excite the electrons.

nomenon is easier to detect with synchrotron-based high-resolution photoemission than with standard XPS.³⁶ In fact, at a photon energy of 380 eV, the emitted electrons have a kinetic energy of 90–95 eV and photoemission probes only the composition of the first 2 to 3 layers in the sample.⁵⁵ Typical results of high-resolution photoemission are shown in Fig. 4. The C(1s) spectrum for O/ZrC(001) exhibits a distinctive line shape with two strong peaks at 283.4 and 281.9 eV. The peak at 281.9 eV is close in binding energy to the single peak found for clean ZrC(001) at 281.7 eV. From the relative intensities of the two peaks it appears that, in O/ZrC(001), a very large fraction ($\sim 40\%$) of the C atoms near the surface has been perturbed by the presence of oxygen. In general, we found C(1s) shifts of 1.3–1.6 eV with respect to the main peak for the substrate. They point either to a strong interaction between O and C atoms (oxygen could be adsorbed directly on top of C sites) or to a O $\leftrightarrow$ C exchange which could take place in the surface (Zr–C bonds being replaced by Zr–O and C–C bonds). These two possibilities will be examined in Sec. IV using DF calculations. In Fig. 4, the C(1s) spectrum for O/VC(001) is characterized by essentially a single peak at 282.1 eV and a very small feature near 283.5 eV. For clean VC(001), the C(1s) peak shows up at 282.0 eV. Thus it appears that the O $\leftrightarrow$ C interactions are negligible in O/VC(001). The results of photoemission are consistent with data of HREELS for O/VC(001).²¹ The C(1s) spectra in Fig. 4 suggest a big difference in the mechanisms for the oxidation of ZrC(001) and VC(001). The first-principles calculations presented in the next section also corroborate this finding. The calculated ΔE 's for the oxidation processes indicate that two reaction paths are possible for the C $\leftrightarrow$ O exchange in O/ZrC(001), while only one is allowed in O/VC(001).

IV. OXYGEN ON ZrC(001) AND VC(001): DENSITY FUNCTIONAL STUDIES

A detailed theoretical study of the structural parameters for the clean ZrC(001) and VC(001) surfaces is presented

FIG. 5. Side view of atomic displacements for the ZrC(001) and VC(001) surfaces (Ref. 25). The C atoms are represented as the darker gray spheres.

elsewhere.²⁵ Here, we only summarize the main features which are relevant to the present study. The DF results show some surface relaxation in the transition metal carbide surfaces: the topmost C atoms displace outward and the Zr or V atoms inward with respect to the truncated bulk atomic positions (see Fig. 5). Table I lists the calculated amplitudes for this rippling (R in Fig. 5). The three different methods used in this study, all electron (DF-AE) and pseudopotential (DF-PSP) or frozen-core (DF-PAW) calculations, indicate that the rippling is of ~ 0.07 Å in ZrC(001) and ~ 0.18 Å in VC(001). In general, these values are consistent with the results of other theoretical works.^{25,56,57} Rippling has been observed in several experimental and theoretical studies for metal carbide surfaces.^{13,14,18,23,25,56–58}

For the bulk carbides, recent DF calculations show a metal $\rightarrow$ carbon charge transfer ($\sim 1.3 e$ in ZrC and $1.0 e$ in VC).²⁵ At the ZrC(001) and VC(001) surfaces, the metal atoms have a positive charge but the metal-carbon bonds still exhibit a strong covalent character with Zr(4d)–C(2p) and V(3d)–C(2p) hybridizations.²⁵ The moderate positive charge on the metal centers (0.8 – $1.1 e$) is not large enough to prevent a metal $\rightarrow$ oxygen electron transfer. In other words, the metal can be further oxidized. On the other hand, the outward position of the C atoms in the ZrC(001) and VC(001) surfaces suggests that they may play an important role in the oxidation process. The highest occupied electronic states have a strong carbon character in the case of ZrC(001), see top of Fig. 6, but in the case of VC(001) the extra electron in the valence band resides predominantly in a V(3d) level,²⁵ bottom of the same figure. Thus on the basis of these struc-

TABLE I. Surface rippling (Å) in ZrC(001) and VC(001): First-principles results.^a

	DF-PSP ^b	DF-PAW ^c	DF-AE ^d
ZrC(001)	0.08	0.09	0.05
VC(001)	0.19	0.17	0.17

^aFor a definition of the rippling (R) see Fig. 5.

^bCalculations using the RPBE functional, core pseudopotentials, and a plane wave basis set (DF-PSP).

^cCalculations using the PW91 functional, core electrons represented by the projected augmented wave method, and a plane wave basis set (DF-PAW).

^dCalculations using the RPBE functional, including all the electrons with a numerical basis set (DF-AE).

FIG. 6. DF-PSP calculated density-of-states for ZrC(001) and VC(001) surfaces.

tural and electronic properties, it is difficult to make an *a priori* prediction of the relative strength of the $O \leftrightarrow C$, $O \leftrightarrow Zr$, and $O \leftrightarrow V$ interactions.

We examined the bonding of O atoms to the following adsorption sites of the ZrC(001) and VC(001) surfaces: on top of Zr or V, on top of C, bridging two metal or two C atoms, bridging metal and carbon atoms and threefold hollow sites including either two metals and one carbon or two carbons and one metal atoms. The oxygen overlayer was in a

$p(2 \times 2)$, $p(2 \times 1)$, or $p(1 \times 1)$ array with respect to the lattice of Zr or V surface atoms. The geometry of the adlayer and carbide surface two outermost atomic layers was always fully relaxed. Tables II and III display a summary of the DF results. The energy released by the bonding of O atoms to the carbide surfaces is more than enough to dissociate the O_2 molecule³⁶ and the $O_{2,gas} \rightarrow 2O_{ads}$ reaction is very exothermic (>3 eV). The DF-PSP, DF-PAW, and DF-AE calculations for O/ZrC(001) revealed that O adsorption directly on top of C and on bridge sites (Zr–Zr or C–C) was unstable and the adatoms spontaneously moved onto the kind of CZrZr hollow sites shown in Fig. 7. The off center site found here is logical because of the different atomic radii for Zr and C.⁵⁹ Our first-principles calculations indicate that this is by far the most stable adsorption site for O on ZrC(001). These theoretical results are consistent with photoemission experiments (Fig. 4) that point to a strong $O \leftrightarrow C$ interaction in the oxygen/ZrC(001) interface, but the DF calculations complement the experiment by revealing a more complex situation since the adsorbate is bonded simultaneously to both C and Zr (Table III). In contrast to the description above for O/ZrC(001), for the interaction of O with the VC(001) surface the DF calculations show no big differences for the O adsorption energies on top of V and on a CVV hollow. Hence the $O \leftrightarrow V$ interactions are stronger than the $O \leftrightarrow Zr$ interactions, and from this one may deduce that the $O \leftrightarrow C$ interactions are not really essential for the binding of the adsorbate in O/VC(001). Moreover, the VC(001) valence band has one more electron than that of ZrC(001),²⁵ and it occupies states that favor V–O bonding. In Fig. 4, the C 1s spectrum of O/VC(001) exhibits a small shoulder around 283.5 eV. This feature points to a $C \leftrightarrow O$ interaction, as seen in the case of O/ZrC(001), but on VC(001) there is multisite adsorption since the associated energetics does not force the O onto CVV sites.

The results in Table II indicate that the oxygen coverage has a substantial effect on the oxygen adsorption energy. Such a phenomenon is more clearly seen in Fig. 8, which also includes the calculated Mulliken charges⁶⁰ for O adsorbed on the carbide surfaces as a function of coverage (DF-PSP calculations). Due to its large electronegativity,⁶¹ oxygen withdraws electrons from the ZrC(001) and VC(001)

TABLE II. Adsorption energy (eV) of O on ZrC(001) and VC(001): First-principles results.

	ZrC(001)			VC(001)		
	DF-PSP	DF-PAW	DF-AE	DF-PSP	DF-PAW	DF-AE
<i>CMM</i> hollow ^a						
$\theta_O=0.25$ ML	–5.73	–6.45	–5.60	–5.12	–5.11	–4.97
0.5 ML	–4.87	–6.36		–4.68	–5.01	–4.80
1.0 ML	–4.36	–6.30		–4.31	–4.96	–4.47
a-top <i>M</i> ^a						
$\theta_O=0.25$ ML	–3.23	–3.48	–3.31	–5.08	–5.14	–4.91
0.5 ML	–2.92	–3.27	–3.17	–4.71	–5.08	–4.69
1.0 ML	–2.16	–2.49	→ <i>CMM</i>	–4.34	–4.60	–4.25

^a*M* is Zr or V.

TABLE III. Bond distances of O (in Å) on ZrC(001) and VC(001): First-principles results.^a

	ZrC(001)		VC(001)	
	O–Zr	O–C	O–V	O–C
<i>CMM</i> hollow ^b				
$\theta_0=0.25$ ML	2.28 (2.24)	1.40 (1.42)	2.25 (2.18)	1.31 (1.32)
0.5 ML	2.29 (2.26)	1.42 (1.41)	2.25 (2.23)	1.30 (1.31)
1.0 ML	2.29 (2.28)	1.43 (1.41)	2.24 (2.14)	1.32 (1.33)
a-top <i>M</i> ^b				
$\theta_0=0.25$ ML	1.81 (1.87)		1.63 (1.61)	
0.5 ML	1.83 (1.87)		1.64 (1.60)	
1.0 ML	1.82 (1.86)		1.65 (1.63)	

^aCalculations using the RPBE functional, pseudopotentials, and a plane wave basis set (DF-PSP). Results obtained from the PW91 functional, PAW cores and a plane wave basis set (DF-PAW) are given in parenthesis.

^b*M* is Zr or V.

surfaces. This is consistent with experimental measurements that show an increase in the work function of the carbide surfaces upon the bonding of oxygen.³⁹ There is a limit in the number of electrons that the carbide surfaces can provide to an adsorbate, and as the oxygen coverage increases there is a reduction in the negative charge on the individual O adatoms. Another effect that probably reduces the amount of charge transfer for higher coverages is the Coulomb repulsion among the adsorbates. The reduction of the carbide $\rightarrow$ oxygen charge transfer is accompanied by a weakening of the bonding interactions between the adsorbate and the surface, but there is not a linear relationship between the magnitude of the charge transfer and the strength of the adsorption bond. This reflects the strong covalent character in the O–ZrC(001) and O–VC(001) bonds.

FIG. 7. (Color online) Most stable configuration for an O atom on the ZrC(001) surface. Black (red in the web) spheres represent the adsorbate, which is bonded to one C atom (represented as dark gray spheres) and two Zr atoms (represented as light gray spheres).

V. OXIDATION OF ZrC(001) AND VC(001): DENSITY FUNCTIONAL STUDIES

The photoemission spectra described in Sec. III indicate that the adsorption of oxygen can lead to oxidation of the ZrC(001) and VC(001) systems. Using DF-PSP calculations we investigated the energetics of the reactions associated

FIG. 8. Effect of oxygen coverage on the calculated (DF-PSP) adsorption energy and charge of oxygen in O/ZrC(001), solid lines with filled symbols, and O/VC(001), dashed lines with empty symbols.

FIG. 9. (Color online) Initial and final structures for a $C \leftrightarrow O$ exchange in a $ZrC(001)$ surface with an oxygen coverage of 0.5 ML. The O atoms in the unit cell are shown as black (red on the web) spheres. C atoms are represented as dark gray spheres, while light gray spheres denote Zr atoms.

with the oxidation process. In our analysis, only stable initial or final structures were considered and our conclusions will be purely based in thermodynamic arguments and not on kinetics. In a first step, O adatoms could replace the C atoms present in the carbide surfaces. Our DF-PSP calculations indicate that the relaxed geometry arising from this simple exchange of positions between O and C is an exothermic reaction on $ZrC(001)$, $\Delta E = -0.68$ eV at $\theta_O = 0.25$ ML and -0.44 eV at 0.5 ML, with the displaced carbon moving to a $CZrZr$ site and forming a C–C bond (see Fig. 9). In the case of $O/VC(001)$, the DF-PSP calculations predict that a simple $C \leftrightarrow O$ exchange is an endothermic process, $\Delta E = 0.57$ eV at $\theta_O = 0.25$ ML and 0.73 eV at 0.5 ML. This trend is fully confirmed by the DF-PAW calculations. On the basis of the DF calculations, it is clear that the adsorption of O should have a minor impact on the $C(1s)$ spectrum of $VC(001)$, as observed in the photoemission data of Fig. 4. On the other hand, the theoretical results indicate that O adsorption should induce extra features in the $C(1s)$ spectrum of $ZrC(001)$ as a consequence of O–C bonding or the C–C bonding produced by the $C \leftrightarrow O$ exchange. A proper and detailed assignment of the $C(1s)$ features observed in the experimental spectra requires a further analysis which exceeds the scope of the present work. Nevertheless, the experimental and theoretical studies show an important difference in the mechanism for the oxidation of $ZrC(001)$ and $VC(001)$.

The reaction shown in Fig. 9 leads to oxidation of the carbide without changing the relative concentration of oxygen and carbon in the $O/ZrC(001)$ interface. In principle, the C atoms displaced from the surface could react with O adatoms to form gaseous CO_x species.²¹ This is a convenient hypothesis to explain the increase in the $Zr(3d)/C(1s)$ intensity ratio seen in photoemission (bottom panel in Fig. 1). Thus, in the system of Fig. 9(a), the O and C could combine to generate adsorbed CO, see Fig. 10. We found that this reaction pathway was highly endothermic on $ZrC(001)$ and $VC(001)$. For these surfaces, the removal of carbon by a single oxygen atom is essentially impossible. The system in Fig. 10 is unstable due to the presence of C vacancies in the carbide surface. These vacancies can be avoided if the oxygen coverage is large. In the reaction scheme of Fig. 11, two O atoms work in a cooperative way to remove one C atom from the surface. In the $p(2 \times 2)$ cell of Fig. 11(a), there are two O adatoms. One of the oxygen atoms can become embedded into the carbide surface and the displaced carbon

FIG. 10. (Color online) Structure for the formation of CO by reaction of an O adatom with a C atom of the $ZrC(001)$ or $VC(001)$ surface. The O atom is shown as a black (red on the web) sphere. C atoms are represented as dark gray spheres, while light gray spheres denote Zr or V atoms.

reacts with the second oxygen to form adsorbed CO [Fig. 11(b), $\Delta E = -1.26$ eV for $ZrC(001)$ and -0.98 eV for $VC(001)$, DF-PSP]. In the final step [Fig. 11(c)], the CO molecule desorbs [$\Delta E = 0.4$ eV for $ZrC(001)$ and 0.6 eV for $VC(001)$, DF-PSP] leaving behind an oxidized system with a larger metal/carbon ratio than in stoichiometric $ZrC(001)$ or $VC(001)$. The adsorption energies of CO on the oxidized carbides are close to those calculated and measured experimentally for CO on pure $VC(001)$, -0.6 and -0.5 eV,^{23,48} respectively. The CO molecule is not stable on the $VC(001)$ surface at temperatures above 250 K⁴⁸ and, thus, it could not be detected in the photoemission experiments of Figs. 2 and 4.

The results of the DF calculations indicate that the two pathways for the oxidation of the carbide surfaces

are more exothermic for ZrC than for VC , a fact consistent with the trends observed in the photoemission data. The $C(1s)$ spectra and the calculated ΔE 's indicate that pathway (1) plays a minor role during the oxidation of $VC(001)$. For this oxidation process the formation of CO is essential. In $VC(001)$ the C atoms protrude from the surface more than the C atoms in $ZrC(001)$, see Table I. This structural difference does not have a major effect on the chemical behavior of the carbide surfaces, which seems to be determined by their electronic properties, see Fig. 6.

By extrapolating from the behavior found for metal oxides,^{1,3,10} it is frequently assumed that the metal centers in carbide surfaces carry out “the chemistry” and the C centers are simple spectators.^{7,8,26} The type of interactions seen in the $O/VC(001)$ interface are consistent with this assumption, since the C sites in the $VC(001)$ substrate do not play a predominant role in the bonding of O and are not efficient for the bonding of the C adatoms produced by a $C \leftrightarrow O$ exchange. Interestingly, a comparison of the electronic proper-

FIG. 11. (Color online) Formation of CO in a O/ZrC(001) or O/VC(001) interface. In the initial state (a), 0.5 ML of O atoms are located on CMM hollow sites of the surface ($M=\text{Zr}$ or V). Each unit cell contains two oxygen atoms. Then, one of the oxygens inserts into the surface and the other forms CO with the displaced carbon (b). In the final step (c), the CO has desorbed from the surface. The O atoms are shown as dark (red on the web) spheres. C atoms are represented as dark gray spheres, while light gray spheres denote Zr or V atoms.

ties and chemical behaviors of ZrC(001) and VC(001) indicates that the carbide surface with the larger density-of-metal d states near the Fermi level or the smaller positive charge on the metal centers (VC) is not necessarily the more reactive. In ZrC(001), the C atoms are not simple spectators and help to overcome the chemical deficiencies of the metal centers. In the structures of Figs. 7 and 9, the O or C adatoms are si-

multaneously bonded to C and metal surface atoms. A similar phenomenon was seen previously for the O/TiC(001) interface.³⁶ In contrast, preliminary DF calculations for the O/TaC(001) system show a behavior similar in many aspects to that described above for O/VC(001).⁶² Thus the O/ZrC(001) and O/VC(001) interfaces illustrate different types of phenomena that can occur during the oxidation of carbide surfaces.

VI. SUMMARY AND CONCLUSIONS

High-resolution photoemission and first-principles density-functional slab calculations were used to study the interaction of oxygen with ZrC(001) and VC(001) surfaces. Atomic oxygen is present on the carbide substrates after small doses of O_2 at room temperature. At 500 K, the oxidation of the surfaces is fast and clear features for ZrO_x or VO_x are seen in the $\text{O}(1s)$, $\text{Zr}(3d)$, and $\text{V}(2p_{3/2})$ spectra, with an increase in the metal/carbon ratio of the samples. In spite of the substantial oxidation of ZrC(001) and VC(001), no signal was seen for the formation ZrO_2 , VO_2 , and V_2O_5 .

A big positive shift (1.3–1.6 eV) was detected for the C $1s$ core level in O/ZrC(001), indicating the existence of strong $\text{O} \leftrightarrow \text{C}$ or $\text{C} \leftrightarrow \text{C}$ interactions, a phenomenon corroborated by the results of first-principles calculations, which show a CZrZr hollow as the most stable site for the adsorption of O. Furthermore, the calculations also show that a $\text{C} \leftrightarrow \text{O}$ exchange is exothermic on ZrC(001), and the displaced C atoms bond to CZrZr sites. In the O/ZrC(001) interface, the surface C atoms play a major role in determining the behavior of the system.

The adsorption of oxygen induces very minor changes in the C($1s$) spectrum of VC(001). The $\text{O} \leftrightarrow \text{V}$ interactions are stronger than the $\text{O} \leftrightarrow \text{Zr}$ interactions, and $\text{O} \leftrightarrow \text{C}$ interactions do not play a dominant role in the O/VC(001) interface. In this system a $\text{C} \leftrightarrow \text{O}$ exchange is endothermic. VC(001) has a larger density-of-metal d states near the Fermi level than ZrC(001), but the rate of oxidation of VC(001) is slower. The O/ZrC(001) and O/VC(001) systems show two different kinds of mechanisms for the oxidation of carbide surfaces.

The mechanism for the removal of a C atom from ZrC(001) or VC(001) as CO gas involves a minimum of two O adatoms. One to take the place of the carbon in the surface, and the other for the generation of CO. Due to the high stability of ZrC(001) and VC(001), an O adatom alone cannot induce the creation of a surface C vacancy through the formation of CO.

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