Energetics of Oxygen Interstitials in Cr and V

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ABSTRACT

Dissolved oxygen in group IIIA-VA (Nb, Ti, Zr, Y) based alloys is a fundamental problem, affecting both mechanical properties and oxidation resistance, yet details of the phenomenon are poorly understood. In these alloys, oxygen is more stable dissolved in the metal than as an oxide-compound. In contrast, alloys based on Ni, Fe, Al and Cr exhibit almost no oxygen solubility. To improve the performance of Nb and Ti based alloys it is necessary to understand the differences in oxygen solubility between these two groups of metals. As a first step we considered the energetics of interstitial oxygen in α-V and α-Cr. Both of these metals have a BCC structure, yet the oxygen solubility in V is much higher than that in Cr. We obtain total energies, densities of states and population analyses using the CASTEP plane-wave pseudopotential density functional computer code. The differences in the energetics and electronic structures of the two materials, particularly the partial densities of states associated with the interstitial oxygen, are discussed.

INTRODUCTION

The use of alloys in high temperature oxidizing atmospheres relies on the formation of a continuous oxide layer on the surface, separating it from the environment and limiting the oxidation reaction rate. Useful oxide compounds (e.g., Cr_2O_3, Al_2O_3 and SiO_2) must have slow oxygen transport kinetics, but this is not the only criterion required. The oxide must form on the alloy surface and the alloy-scale interface must approach a condition of equilibrium. The first is a function of composition and transport kinetics, while the second is purely thermodynamic and requires that the alloy is saturated with oxygen. For Ni and Fe based alloys this does not present a problem as oxygen is more stable as an oxide and the concentration required for saturation is below levels that affect mechanical properties. In contrast, oxygen is more stable dissolved in group IIIA-VA (Nb, Ti, Zr, Y…) based alloys; oxygen concentrations of 2 to 10 at% are required for saturation and these levels are detrimental to mechanical properties. To maintain bulk mechanical properties oxygen concentration needs to remain below saturation levels, which results in a steady state condition at the alloy-scale interface where oxide is reduced and oxygen continually diffuses into the alloy. This issue needs to be addressed before suitable oxidation behavior can be obtained for these alloys.

The oxygen saturation limit is determined by the stability of the oxide compound and the stability of dissolved oxygen in the alloy. As the oxide compound is typically fixed by the required transport kinetics the stability of dissolved oxygen is the fundamental issue. Therefore, it would be interesting to gain a better understanding of the stability of oxygen in these metals. Neutron diffraction studies show that oxygen atoms randomly occupy octahedral sites in BCC Vanadium [1], with similar behavior assumed for Cr. In this work, the energetics of interstitial oxygen in pure α-V and pure α-Cr are considered. Both of these metals are BCC, yet their oxygen solubilities are very different, with that of V being much higher than that of Cr. We obtain total energies, densities of states and population analyses using the CASTEP plane-wave pseudopotential density functional computer code. We investigate the energetics of both bulk interstitials, and interstitials near Cr and V (001) surfaces. The differences in the energetics and electronic structures of the two materials, particularly the partial densities of states (PDOS) associated with the interstitial oxygen, are discussed.

RESULTS AND DISCUSSION

The calculations described in this paper were performed using the CASTEP ab initio computer code [2]. CASTEP is a plane-wave pseudopotential code based on density functional theory [3]. The calculations were carried out using ultrasoft pseudopotentials [4], the generalized gradient approximation (GGA) to the local density functional of Perdew, Burke and Ernzerhof [5], and Gaussian smearing and Pulay density-mixing. Because of the large size of the supercells used (as described below), the Brillouin zone was sampled using only a small number of k-points, typically one or two. The calculations produce total energies, electronic structure information including band structure and total and partial densities of states, and population analyses. All calculations were performed without atomistic relaxation.

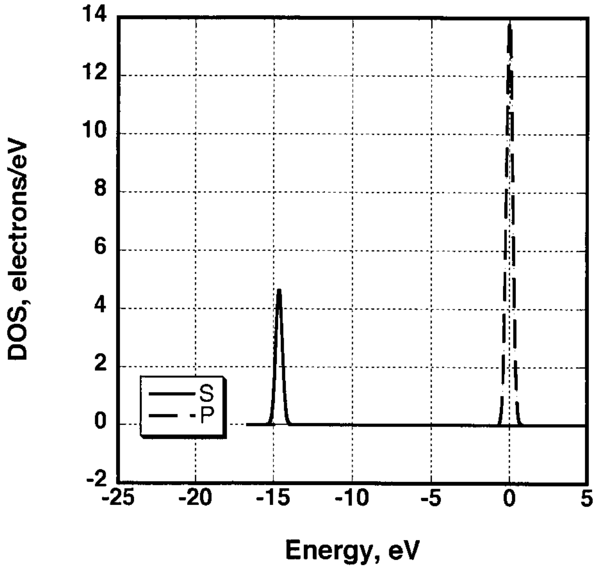


Figure 1. Partial density of states of atomic oxygen.

Two sets of calculations were performed. In the first set, the energies of interstitial oxygen located on octahedral sites in bulk V and Cr were computed. In the second set, similar calculations were carried out on interstitials located in the topmost four layers of V and Cr cells with (001) surfaces exposed.

The formation energy of an interstitial, as computed here, is the difference in energy between a computational cell containing the defect, and the sum of the energies of the defect-free cell and an oxygen atom in its reference state. Typically, the reference state for oxygen is diatomic O_2 at atmospheric pressure. In this work, however, we choose atomic oxygen as the reference state. At low oxygen pressures where oxides are not stable, atomic oxygen is the dominant vapor species, and the species that dissolves in the metal.

So as to maintain consistency with our other calculations, we compute the energy of atomic oxygen using CASTEP. Because CASTEP is a periodic code, we perform this calculation using a cubic lattice having a fictitiously large lattice constant of 10 angstroms, and take the energy and density of states to be representative of those of the appropriate reference state. The single-atom total energy computed in this manner is –431.097 eV. The density of states (as shown in figure 1 above) exhibits two peaks corresponding to the bonding s and p levels, with the p peak located at the Fermi energy (the energy zero of the PDOS plots) and the s peak about 15 eV lower. The separation of the peaks is consistent with Hartree-Fock calculations of the 1s and 1p level separation in atomic oxygen [6], indicating that our chosen reference state is reasonably close to that configuration.

The formation energies of bulk octahedral interstitials were computed using 2x2x2 BCC periodic supercells of V and Cr, with a single oxygen atom placed at an octahedral site, corresponding to an oxygen concentration of 5.9at%. These energies were computed and compared with the sum of the energies of the oxygen-free supercells and atomic oxygen. The formation energies for the V and Cr interstitials were –29.62eV and –13.62eV, respectively. While the magnitudes of these energies depend on the reference state oxygen energy, the signs indicate that octahedral interstitials are stable in both metals, and are significantly more stable in V than in Cr. Oxygen partial densities of states for the interstitials are shown in figures 2a and 2b. In both metals, the oxygen PDOS is structurally the same; the p level shows a splitting not evident in the atomic oxygen PDOS, and the bonding levels are lower with respect to the Fermi energy for Cr than for V. The splitting is likely due to a change in local symmetry for the octahedral interstitial compared with the isolated atom reference state. The separation between s and p levels is similar to that in the reference state. While the magnitudes of the formation energies may change when atomistic relaxation is included, we do not expect a reordering of the relative stabilities of the V and Cr interstitials.

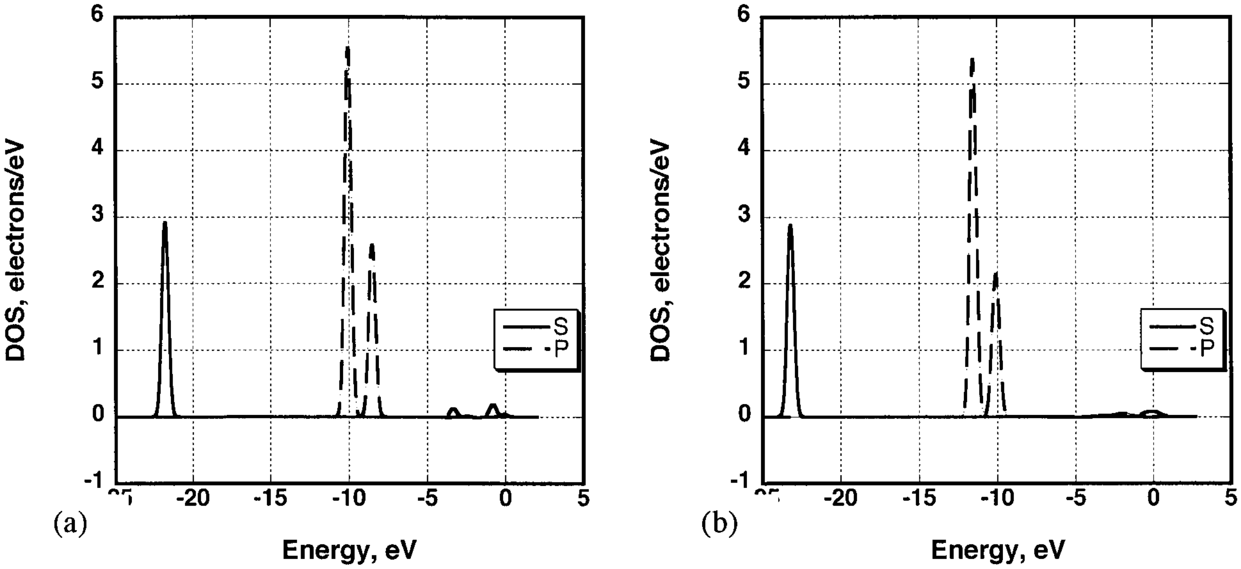


Figure 2. Partial density of states of bulk oxygen interstitial in (a) V, and (b) Cr.

In addition to the stability of bulk oxygen interstitials, other energetic issues are important in the consideration of the details of oxygen diffusion. In general, the energies of defects near a surface will be different from those of defects in the bulk. In addition, to understand the dynamics of interstitial diffusion, the energy barriers along likely diffusion paths need to be computed. Finally, the presence of substitutional alloying elements may have a significant effect on oxygen diffusion.We address the first of these issues below; calculations of diffusion barriers, and of the effects of substitutional alloying elements, are currently under way in our laboratory.

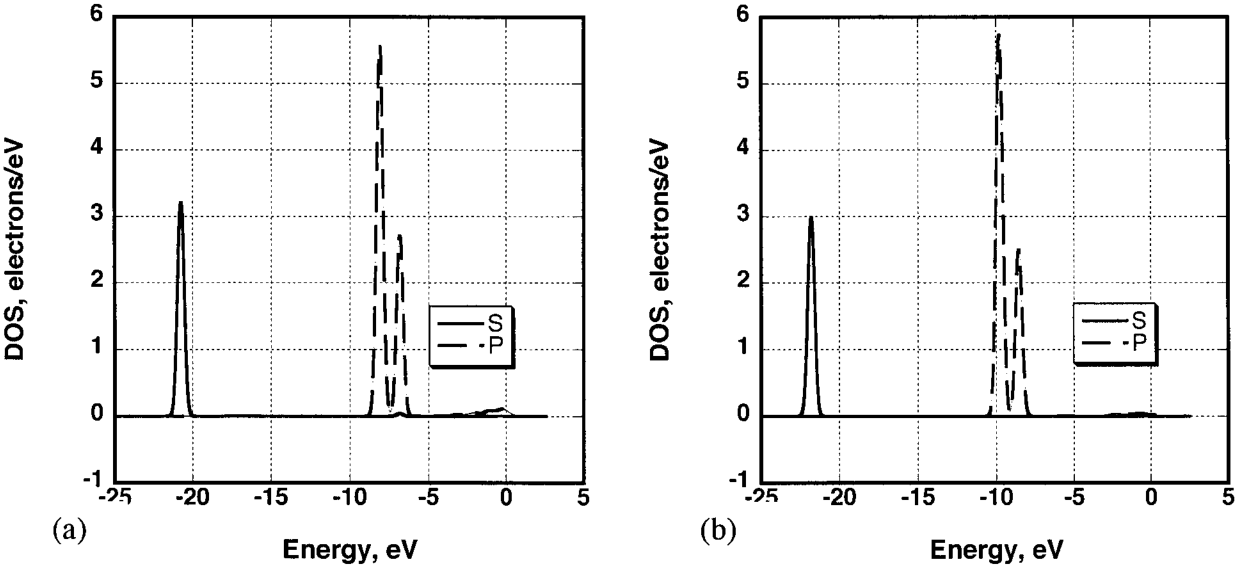
We compute the relative energies and PDOS for octahedral oxygen interstitials located in the first four layers of 2x2x4 supercell periodic slabs with the (001) surface exposed. Results are shown in Table 1; for both metals, the zero of energy is taken to be the energy of the interstitial in the first layer.

Table I. Energies and partial charges of oxygen interstitial in V and Cr.

Layer	Energy, V (eV)	Energy, Cr (eV)	Charge, V (e)	Charge, Cr (e)
1	0.0	0.0	-0.54	-0.48
2	3.16	5.66	-0.34	-0.27
3	2.96	6.23	-0.39	-0.30
4	2.55	6.26	-0.39	-0.30

For both metals, the energy of the interstitial in the first layer is lower than those of interstitials in layers further from the surface. This suggests that at low concentrations, the interstitials will be primarily confined to the first layer. The energy cost to create an interstitial in the second through fourth layers is larger for both metals, and is larger for Cr than for V, which is consistent with the lack of solubility of O in Cr. It is also worth noting that the energies of second-layer interstitials for both metals are substantially the same as those of third- and fourth-layer interstitials, indicating that effective bulk conditions are attained close to the surface. This conclusion is supported by the values of the oxygen partial charges, obtained via Mulliken population analysis [7], also shown in Table I.

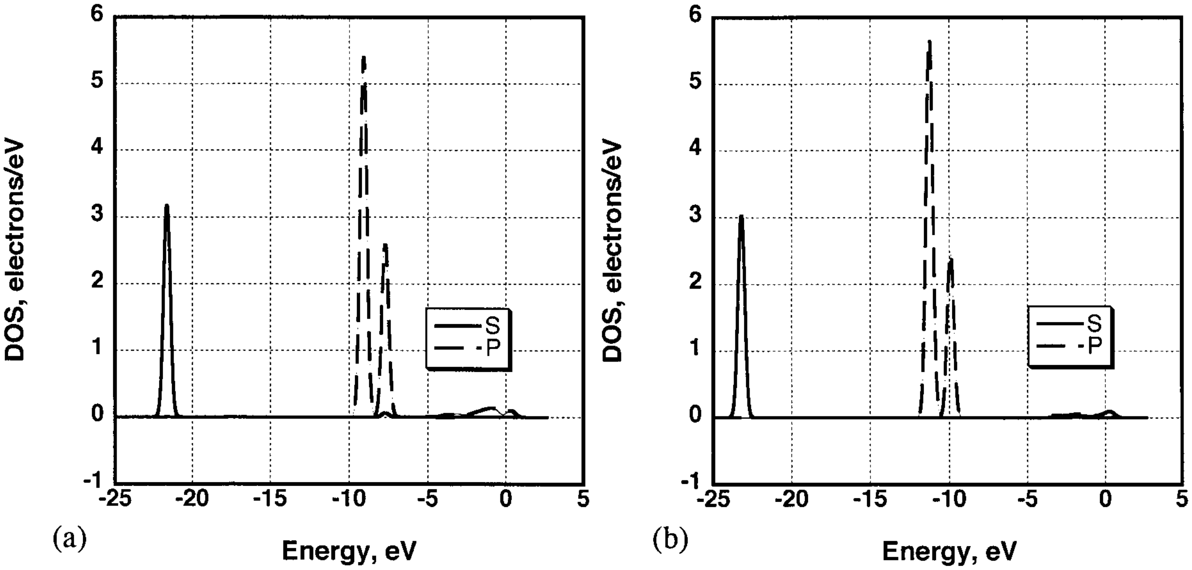
The oxygen PDOS for interstitials in the first and fourth layers are shown in figures 3a-b and 4a-b for V and Cr, respectively. The PDOS structures for all layers resemble that of the bulk interstitials, except that the PDOS of the first-layer interstitials is closer to the Fermi energy by approximately 3eV, again indicating that bulk conditions exist relatively close to the surface.



(a)

(b)

Figure 3. Partial density of states of oxygen interstitial in V. layer 1, (a) and layer 4 (b).



(a)

(b)

Figure 4. Partial density of states of oxygen interstitial in Cr. layer 1, (a) and layer 4 (b).

CONCLUSIONS

Ab initio calculations of the energetics of octahedral oxygen interstitials in BCC V and Cr are consistent with the known oxygen solubility of these materials at low concentrations. Bulk interstitials in both V and Cr are found to be stable, with the V interstitial being substantially more favorable energetically than the Cr interstitial. For interstitials near (001) V and Cr surfaces, it is energetically favorable for isolated interstitials to exist in the first layer; in layers further from the surface, the energies converge within another layer or two to values higher than those of surface-layer interstitials, indicating that bulk conditions exist to within a couple layers of the surface. The energy cost of placing an interstitial in the second layer, versus the first layer, is larger for Cr than for V. The magnitudes of the energies involved will change when atomistic relaxation is included, and such calculations are ongoing.

The energy profile of interstitial energy with depth is not a complete picture of the energetic factors that limit diffusion into these materials. Also of concern is the height of the energy barrier that controls the likelihood of an oxygen atom hopping to a neighboring octahedral site. Accurate calculations of this barrier involve a relaxation of the neighboring atoms adjacent to the reaction path; such calculations are presently being carried out.

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