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A first-principles study of dilute solutions of oxygen in titanium

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Solutions of oxygen in titanium are investigated through density functional calculations. This method provides an accuracy comparable to the experimental determination of the enthalpy of dissolution of O in α-Ti but not for β-Ti solutions. The insertion of an O atom induces an increase in the electronic density around the O atom and a diffuse decrease in the electronic density in the lattice. Two oxygen sites sharing a face of two adjoining Ti octahedra cannot be simultaneously occupied.

Keywords: Ab initio calculation; Titanium; Interstitials; Oxidation; Thermodynamics

The rapid development of nanostructured Ti-based materials [1] has been impressive in recent years. The use of multiscaling simulations, which is the most appealing approach for the study of these materials, requires the availability of reliable ab initio methods to deal with defects. In the first part of this paper, we shall discuss mainly the ability of ab initio methods to determine the enthalpy of formation of defects. This point is timely as the calorimetric methods that are most suitable [2] for determining the formation enthalpies of defects in metal–oxygen systems are less and less available. In the second part of this paper, we shall examine the geometric and electronic perturbations caused by the insertion of an O atom in Ti. We have used the Vienna Ab initio Simulation Package (VASP) [3,4] which is based on the density functional theory. Technical choices made in the use of this package have been detailed elsewhere [5,6]. A cutoff energy for the plane-wave basis equal to 400 eV has been chosen. We have considered 10 valence electrons for Ti and six valence electrons for O.

As it is stable up to 1152 K [7], the hexagonal close-packed (hcp) structure (α phase) is the easiest Ti structure to study using a DFT program at 0 K. We have used two supercells: an orthorhomboedron with 48 Ti atoms (four layers of 12 atoms) and a hexagonal prism with 64 Ti atoms (four layers of 16 atoms). In both cases, the product of the number of k points time the number of Ti atoms has been chosen equal to 384. We have calculated the energy minima for both Ti_n and Ti_nO supercells under the hexagonal compact symmetry constraint, allowing the parameters a and c to vary independently. For both supercells, the atomic volume of pure Ti has been found equal to 17.28 Å^3 with $c/a = 1.58$ in agreement with experiments [8] instead of the ratio 1.633 expected for ideal hcp structures. This implies that the octahedra are not quite regular: the lengths of the edges are either 2.87 or 2.93 Å. The incorporation of one O atom in our supercells provokes a moderate lattice expansion corresponding to a partial molar volume of O equal to 2.6 cm^3. The Ti–O distance, which is equal to 2.05 Å in the unrelaxed crystal, increases by 0.03 Å. This result differs from the statement of Lado-Tourino and Tsobnang [9] who find that relaxation provokes a decrease of the Ti–O distance.

As detailed in Tétot et al. [10], two calibration methods have been used, yielding slightly different results, the so-called chemical calibration being probably more accurate. As it will be discussed later, the choice of a reference state plays an essential role in the ability of local density approximation (LDA) and generalized gradient approximation (GGA) functionals to calculate the energies of formation of defects, and so we present them in detail. As shown in Table 1, three processes may be considered to describe the oxidation process. Process (A), which considers the reaction of atomic O with Ti is

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Table 1. Calculated vs. experimental heat releases for the three processes considered

Process	Experiment (chemical calibration)	GGA calculation at 0 K	Difference LDA–GGA
$\frac{1}{x}\mathrm{Ti} + \mathrm{O} \rightarrow \frac{1}{x}\mathrm{TiO}_x$	−9.01	−8.82	−1.37
$\frac{1}{x}\mathrm{Ti} + \frac{1}{2}\mathrm{O}_2 \rightarrow \frac{1}{x}\mathrm{TiO}_x$	−6.50	−5.75	−0.75
$\left(\frac{1}{x} - \frac{1}{2}\right)\mathrm{Ti} + \frac{1}{2}\mathrm{TiO}_2 \rightarrow \frac{1}{x}\mathrm{TiO}_x$	−1.45	−1.08	−0.25

Process (A) (atomic O reference), process (B) (reference O_2), process (C) (comproportionation). Energies are in eV.

the more direct one. We shall use it in the discussion of the oxidation of β-Ti. The heat effect associated with process (B) is half the partial molar enthalpy of mixing of O_2 ($\Delta H(O_2)$) and is the quantity which is measured in the high-temperature calorimeter. The heat effect associated with process (C) may be written:

$$1/2\left[\Delta H(\mathrm{O}_2) - \Delta_\mathrm{f} H^0_T(\mathrm{TiO}_2)\right] \qquad (1)$$

In this expression, $\Delta_\mathrm{f} H^0_T(\mathrm{TiO}_2)$ is the formation enthalpy of TiO_2 at temperature T. This quantity is only weakly temperature dependent as the number of oscillators remains constant in the transformation (C) while the number of gaseous species remains zero. This is not the case for processes (A) and (B). Results are reported in Table 1 and in Figure 1.

As pointed out by Crocombette et al. [11], interstitial O is easier to form with LDA than with GGA. Our simulations confirm this result in this particular case. The discrepancies between LDA and GGA strongly decrease when both reference states are condensed phases. This feature was also present in the study of O solutions in Si [5]. Moreover, the agreement with experiment is very good when the comproportionation process is used. It is noteworthy that the relaxation energy is rather small (0.085 eV).

Now let us turn to β solutions. In the interest of simplicity, we have used process (A) which uses atomic O as a reference and GGA functionals to study the dissolution of O in β-Ti. In spite of its metastability at low temperatures, no difficulty occurs for pure β-Ti which can be relaxed at 0 K without loss of the initial symmetry of the crystal. The energy of transition per atom at 0 K β to α is found to be somewhat more exothermic (−0.104 eV) than the experimental value of −0.045 eV at 1152 K determined by Kaschnitz and Reiter [7].

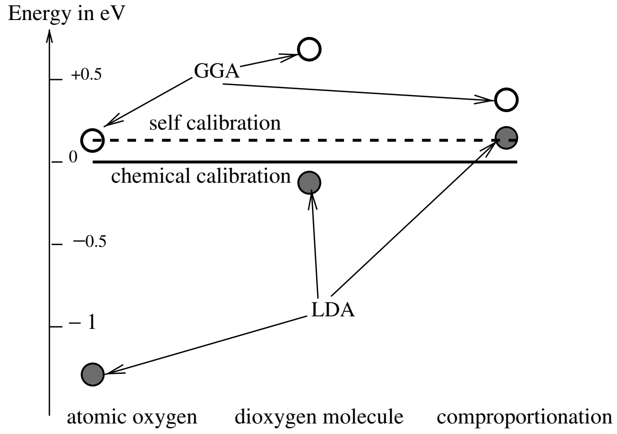

Figure 1. The difference between the experimental and calculated heat of reactions for solutions of O in α-Ti as a function of the approximation (GGA vs. LDA) and of the reference state. Negative values indicate a more exothermic O dissolution than experimentally observed.

Things are quite different for O solutions: The insertion of O breaks the initial symmetry and makes the transition towards a more stable phase easier. If no relaxation is allowed, the insertion of O is found to be exothermic but with a heat release (5.52 eV) much smaller than found in α phase (8.74 eV). This is not too surprising because of the unfavorable values of the Ti–O distances (two values equal to 1.63 Å and four other ones equal to 2.30) in the flattened octahedrons of the body-centered cubic (bcc) lattices compared to the six Ti–O distances equal to 2.05 Å in the α phase.

Full relaxation cannot lead to the α phase since the applied supercells for the β phase are not commensurate with the α phase.

In fact, what we obtain in our simulations are structures intermediate between α and β structures: in order to ascertain this point, we have relaxed at constant volume several supercells with different numbers of Ti atoms under the cubic symmetry constraint. In any case the calculated heat effect is intermediate between:

- The expected value for the β phase ($-9.12\ \mathrm{eV\ mol}^{-1}$). This value is obtained from Table 1 by adding the experimental difference of $\frac{1}{2}\Delta$ H(O_2) in the α and β phases. (−0.30 eV) to the calculated GGA value for the α phase.
- The heat released from a two-step unrealistic process.
  1. Transformation of the whole sample from β structure to α structure (martensitic transformation). This step corresponds to a heat release equal to $n_{\mathrm{Ti}} \cdot \Delta H$ transition.
  2. The dissolution of O in α-Ti: $\frac{1}{2}\Delta H(\mathrm{O}_2)$.

These quantities have been reported in Table 2. If the O is removed from the sample, it is noteworthy that the final energy per Ti atom (after relaxation) is smaller than the initial energy of pure β-Ti by an amount independent of the size of the sample as long as we are using a supercell with $8n$ Ti atoms (with $n = 1, 2, 4, 8$). The calculation using a 54-atom cell provides a somewhat smaller energy decrease.

Let us now examine the electronic perturbation caused by the insertion of an O atom into a Ti lattice (α or β). In order to obtain a picture of the electronic transfer due to the insertion of O, we have used the difference between full self-consistent charge densities ($Ti_{48}O$) on the one hand and superposed self-consistent charge densities of Ti_{48} and of one atomic density for a spinless isolated O atom on the other hand. In the remaining part of this paper, we shall call this quantity $\Delta\rho$. The essential feature is an enhancement of the electronic density in the vicinity of the O atom which pro-