

First-principle study of the of oxygen behaviour in γ -TiAl

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Abstract

New TiAl-based alloys, as for instance the γ -TiAl intermetallic, are adopted for the last generation turbomachines in aerospace industry and their use is likely to increase in the future¹. In this evolution, the environmental conditions will move to higher temperature and pressure conditions. The oxidation behaviour is therefore essential for such applications and it has been studied in the past². However, fundamental data, as the diffusion coefficients of oxygen in these materials, are missing. The aim of this work is to derive these quantities from *ab initio* methods.

γ -TiAl crystallizes in the $P4/mmm$ space group and it can be seen as built by two structural units, constituted by octahedra, respectively made of 4Al+2Ti and 4Ti+2Al atoms. These sites are herein labelled as $[Ti_2Al_4]$ and $[Ti_4Al_2]$. The accommodation of O atoms in the centre of these octahedra has been investigated by *DFT* calculations performed with the *VASP*³ code, using the projector augmented wave pseudopotential and the GGA approximation. Vibrational properties and interatomic forces constants were obtained by the finite displacement method, using the *phonopy*⁴ code. The results indicate that oxygen is not stable in the octahedral sites and that, when the structure is fully relaxed, it moves toward two other interstitial sites (Figure 1): the first, named α , corresponds to the Al-Al corners in $[Ti_2Al_4]$; the second, named β , is obtained by a shift along the z direction, toward the top or the bottom of the $[Ti_4Al_2]$ octahedral centre. The latter is the site with lowest energy.

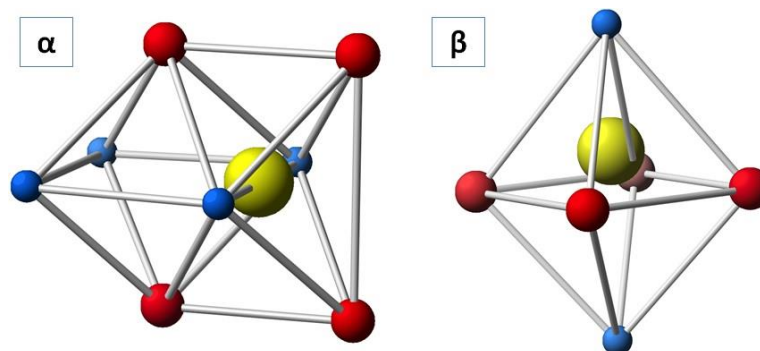


Figure 1. α and β interstitial sites occupied by oxygen (yellow) in γ -TiAl (Al in blue, Ti in red).

The atomic mechanism behind the diffusion of oxygen atoms in γ -TiAl were then studied using the Nudged Elastic Band (NEB) method as implemented in VASP³. This allowed identifying the minimum energy paths (MEPs) for the jumping of oxygen through the interstitial α and β sites and the relative barrier energies. Our results indicate that the diffusion of oxygen in γ -TiAl is a complex process, which includes several steps. For each of this, the jumping rate ν was computed according to the transition state theory⁵ as:

$$\nu = \nu^* e^{-\Delta E/kT}$$

where ΔE is the barrier energy, T is the temperature, k is the Boltzmann constant and ν^* is referred as an *attempt frequency*, which can be obtained from the phonon bands computed at the saddle point and the starting point of the MEP. Finally, the analytical multistate diffusion method⁶ was applied to obtain the diffusion coefficients in the different crystallographic directions and the results are shown in Figure 2.

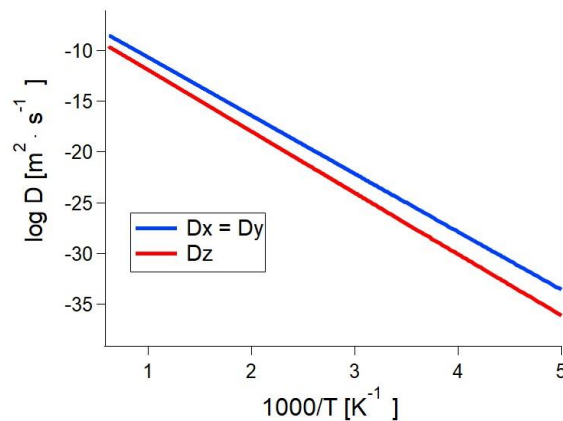


Figure 2. Diffusion coefficients in the basal plane (blue) and in the z direction (red).

The results indicate generally low diffusion coefficients and a clear anisotropy between the basal plane ($D_x = D_y$) and the z direction, with diffusion being faster in the former.

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