

Interstitial diffusion in a tetrahedrally close packed structure: oxygen diffusion in β -tungsten

The diffusivity of interstitial atoms in complex structures has received scant attention and very little is known experimentally. Here, the particular case of interstitial oxygen in tungsten is considered, both for tungsten in the usual bcc structure and in the A15 structure.

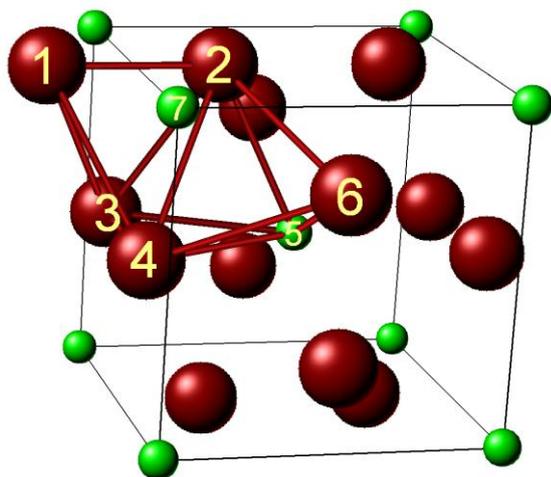


Figure 1 A15 structure, small green (large red) spheres represent 12 (14) - fold coordinated atoms. Tetrahedra are formed by atoms labeled 1,2,3,4; 2,3,4,5; 2,4,5,6 and triangles which bisect triangular bipyramids are formed by atoms labeled 2,3,4; 2,4,5; 3,4,5; and 2,4,6. Note that no interstitial atoms have been displayed.

Achieving metallic materials with good properties almost always involves processes in which diffusion plays an essential role. In recent years modelling diffusion in the most commonly observed simple structures, such as dilute solid solutions with fcc and bcc crystal structures, has been quite successful [1]. Generally, starting from ab initio electronic density functional methods a fair agreement with experimental data can be achieved. Even the presence of dislocations and other structural imperfections has been modelled with apparent success [2]. Diffusion in complex crystal structures is still rather poorly understood because there are many possible mechanisms through which diffusion can occur. Here, we consider the simplest complex structure, the so-called A15 structure which occurs for compounds such as Cr_3Si and also for W when a few percent of interstitial N, O or F is dissolved. We select this particular structure because it is the simplest representative from the class of tetrahedrally close packed structures which features in many intermetallic compounds. A particularity of this class of structures is that tetrahedra between nearest neighbor atoms entirely fill the whole crystal volume.

Therefore, in spite of the structural complexity, the candidate locations for sufficiently large interstitial atoms is easily guessed to be either the centers of these tetrahedra or the centers of the triangles where two tetrahedra touch one another. In the A15 structure there are just 3 crystallographically distinct tetrahedra and just 4 distinct triangular bi-pyramids, see figure 1. Thus there are just 7 likely positions for interstitial species. Closer examination by means of ab initio electronic density functional calculations of these 7 positions revealed that for interstitial oxygen in tungsten with the A15 structure, so-called β -W, there are just two energy minima among the 7 candidate positions: the center of tetrahedron 2,3,4,5 is a local energy minimum about 0.75 eV above the global energy minimum at the center of triangle 2,4,6; while the other positions are either saddlepoint configurations (1,2,3,4 and 2,4,5) or not being associated with energy extrema at all (2,4,5,6; 2,3,4; 3,4,5). Furthermore, when these positions are connected, it is easy to show that there are only three pathways which give rise to diffusion through the crystal. These three pathways can be represented as sequences of centers of triangles and tetrahedra as follows:

sequence a: $2,3,4,5 \leftrightarrow 2,4,5 \leftrightarrow 2,4,5,6 \leftrightarrow 2,4,6$

sequence b: $2,3,4,5 \leftrightarrow 3,4,5 \leftrightarrow 3,4,5,8$

sequence c: $2,3,4,5 \leftrightarrow 2,3,4 \leftrightarrow 1,2,3,4 \leftrightarrow 1,2,4 \leftrightarrow 1,2,4,7$

where the sequence can be followed in both directions. All interstitial diffusion pathways will consist of sequences a and/or b and/or c. In figure 2 the minimum energy paths for the three sequences are shown. It is immediately evident that the lowest energy barrier of about 1.14 eV occurs for sequence a. Long-ranged atomic transport of interstitial O in β -W is thus possible with an activation energy of just 1.14 eV, as sequences b and c are not required. This energy barrier is of the same magnitude as diffusion activation energies for normal metals (read non-transition metals) in an fcc Al matrix. However it is much higher than the activation energy for interstitial O diffusion in bcc W. In bcc W interstitial O occupies the tetrahedral position. O can move from one bcc tetrahedral interstice to another with an intermediate saddlepoint configuration occurring on the (110) plane. The activation energy barrier is just 0.17 eV. Ignoring the diffusivity prefactor, it follows that interstitial O can diffuse much faster in bcc-W than in β -W. However, when the O concentration exceeds a threshold of 7 atomic percent, bcc-W undergoes a phase transformation to β -W as was recently shown in another study [3]. Therefore, once the phase transformation to β -W occurs, the interstitial O gets trapped, which explains the remarkable stability of β -W, such as in the

case of β -W nanowires which are stable to quite high temperatures [4,5].

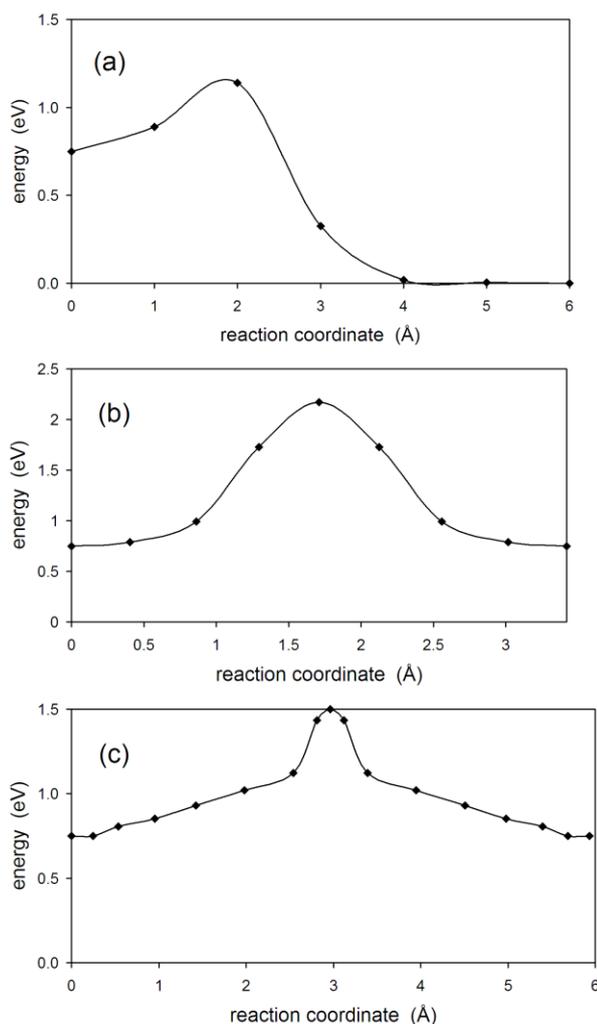


Figure 2 Minimum energy pathways for interstitial oxygen diffusion in β -W according to sequences a, b, and c. Energies are relative to the energy at the center of triangle 2,4,6, the most stable position for an oxygen interstitial in β -W.

As a more general conclusion we find that complex structures provide a range of interstitial positions, some of which are likely to be much more favorable than others. Therefore notable traps for diffusing species are likely to exist. This means that quite generally we can expect diffusivities of interstitial species in complex structures to be rather low in comparison to simpler crystal structures such as bcc and fcc. Diffusion of interstitials into complex phases is thus also likely to be slow which makes that they might not generally provide good sinks or getters, except perhaps at the interface between complex phase precipitates and the bcc/fcc matrix. On the other hand, when interstitials promote the phase transformation towards the complex phase, it is possible that the reverse transformation of complex phase to bcc/fcc phase is slowed down by the tardy process of getting the interstitials out of the complex phase.

References

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Key Words

diffusivity, tetrahedrally close packed, interstitial, tungsten, oxygen

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