First-principles calculations and quantitative imaging of vanadium-oxygen solid solution

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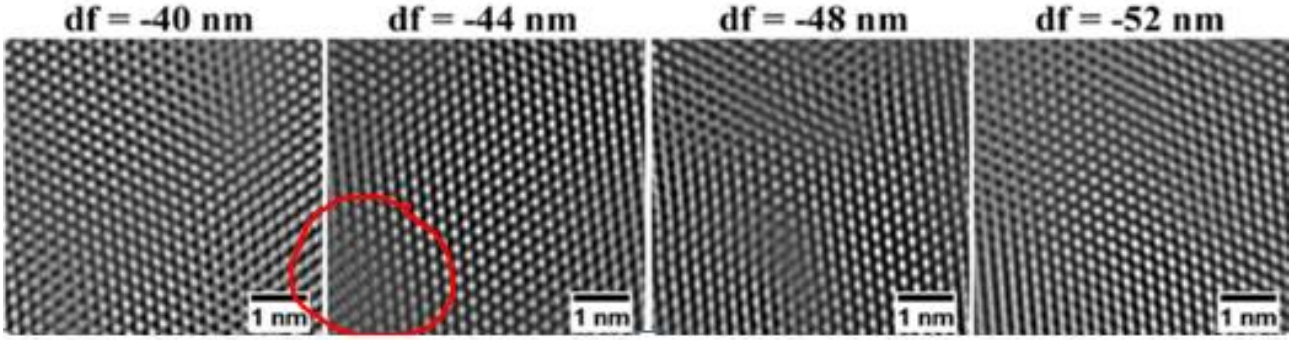
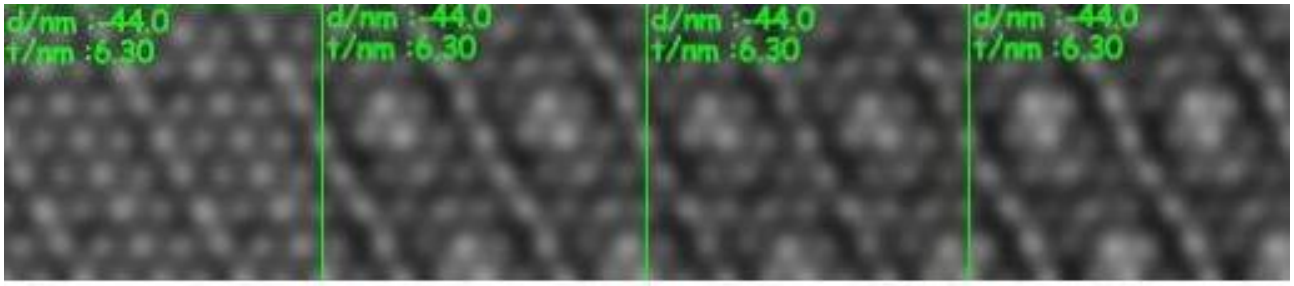
Over the last few years, many international alloy development programmes are focused on vanadium alloy development pertaining to its potential application in fusion power and alternative energy. In fusion applications, vanadium alloys enjoy superiority over other materials due to its superior mechanical and physical properties which can further be tailored by alloying with other transition metals. Vanadium and vanadium-based alloys have also been recognized as storage material for hydrogen and its isotopes with the highest volumetric hydrogen storage capacity in γ-VH2 phase after complete hydrogenation. It also has high affinity towards interstitial impurities such as oxygen, nitrogen and carbon which in due course degrade the mechanical properties. It is essential to understand the interaction of vanadium and vanadium-based alloys with these interstitial impurities to comprehend its effects on the structure, microstructure and in turn mechanical properties of the material.



An intensity delocalization can be clearly observed in the marked region of experimental phase contrast images along [1 1 1] zone axis at different defocus values with thickness ~30nm, at Cs = 0.65 mm and V = 300kV.

According to published literature, oxygen diffuses much faster than carbon and nitrogen in pure vanadium. Introduction of oxygen interstitial in pure vanadium leads to transformation of the system into a body centred tetragonal as a consequence of oxygen dissolution and the presence of significant strain in the crystal. Phase contrast images of vanadium-oxygen solid solution phases reveal intensity delocalization among adjacent columns. Our work is focused on the reason for this observed intensity delocalization and the effects of introduction of oxygen interstitial in pure vanadium lattice. To validate the suggested transformation of vanadium-oxygen solid solution we performed first-principles electronic structure modeling. First-principles density functional theory (DFT) calculations were performed using Vienna Ab-initio Simulation Package (VASP) employing projector-augmented wave (PAW) method. Sufficiently large number of Monkhorst-Pack mesh for k-point sampling and a plane-wave kinetic energy cutoff was set to get converged energy for each supercell. Supercells of pure vanadium and vanadium-containing interstitial oxygen at the octahedral position were constructed and simulated to get accurate atomic forces and stresses. The results obtained from first-principles calculations indicated transformation of vanadium (body-centred cubic) crystal to vanadium (body-centred tetragonal) crystal, also the changes in volumetric strain with respect to oxygen concentration were observed. First-principles calculations suggest that insertion of oxygen interstitial is responsible for the strain induced in the lattice; this strain is maximum near the interstitial and decreases as the distance from the interstitial site increases. We interpreted intensity delocalization between atomic columns as strain in that atomic column and the best possible source for this strain is the presence of interstitial oxygen. To prove how this strain is responsible for intensity delocalization we constructed a model. The model was an artificial vanadium lattice which had a known periodic strain along two adjacent atomic columns. Using JEMS we performed phase contrast image simulations for this lattice employing multislice methodology. Simulated images indicate the intensity delocalization between the strained columns, this intensity delocalization increases with the increasing amount of strain along the columns. The observed intensity delocalization in simulated images also changes with varying defocus and thickness conditions. Details of the structural transformation and intensity delocalization will be presented.



Phase contrast image simulations of V-O model along [111] direction, defocus at -44nm, thickness at 6.3nm, Cs = 0.65 mm and V = 300kV. Increasing intensity delocalization can be seen with increasing strain.