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Impurity migration and effects on vacancy formation enthalpy in polycrystalline depleted uranium

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ABSTRACT

We have used Doppler-broadening of the positron-electron annihilation radiation technique and VASP calculations to verify the previously reported vacancy formation enthalpy H_V^f in polycrystalline depleted uranium. Experimentally we have confirmed a H_V^f of (1.6±0.2) eV . VASP calculations using GGA and LDA approximations gave vacancy formation enthalpies values of 1.98 eV and 2.22 eV respectively. We found residual oxygen in the sample diminished these values by 50% or more. Our new experimental and theoretical data supports the notion that oxygen impurities in the sample are responsible for lower values of vacancy formation enthalpies. Measured and calculated vacancy formation enthalpies, as well as the obtained oxygen migration enthalpy of (0.6±0.1) eV, are compared and discussed with values reported in the literature.

1. Introduction

Metallic uranium and various uranium oxides have been studied with theoretical and experimental techniques to better characterize the elemental properties. Pure uranium has three phases from ambient temperature up to its melting point of 1407K [1-3] (see Table 1). The γ phase of uranium is stable only at high temperatures and is thermodynamically unstable at low temperatures [4]. When alloyed with Zr or Mo, the bcc γ phase can become stable at lower temperatures. A stable γ phase is desired for reactor engineering and design due to its isotropic swelling behavior[4, 5].

Positron annihilation spectroscopy (PAS) techniques have been used to characterize defect properties in uranium. Doppler-Broadening of the Annihilation Radiation (DBAR) enables calculations of vacancy concentration and formation enthalpies [6, 7]. Matter *et al.* [1] and Kögel *et al.* [2] studied relatively large cylinders (3451mm^3 for Kögel and 3015mm^3 for Matter) of polycrystalline uranium samples. After annealing to remove stresses, strains, and impurities, they employed DBAR to extract the vacancy formation enthalpy. Both authors observed discontinuities in their data at phase transition temperatures but with differing values in their measured enthalpies; Matter *et al.* is 400% larger than that measured by Kögel *et al.*

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As suggested in our previous work [8], it is possible the discrepancies between the two measured vacancy formation enthalpies could be due to the oxygen impurities remaining in their larger samples.

Table 1. Uranium Phases

Phase	Temperature(K)	Structure	Volume (Å^3)
α	Up to 941	Orthorhombic	83.005±0.003
β	941-1048	Tetragonal	654.716±0.003
γ	1048-1407	Body Centered Cubic	43.763±0.006

In fact, Matter briefly discussed that the impurities in his sample would generally lead to an enthalpy value smaller than for the pure metallic uranium. With this understanding, he estimated the true value of the formation enthalpy would lie somewhere between 1 to 1.3eV.

High-resolution X-ray photoelectron spectroscopy (XPS) by Senanayake *et al.* [9] shows a decrease in the oxygen and uranium binding energy, along with an increase in the rate of oxygen diffusion from the bulk to the surface, at temperatures greater than 400K. Our group reported an increase in the DBAR line shape parameter between 400 and 500K for a uranium sample with an oxide surface layer [8], indicating increasing vacancies due to oxygen desorption from the bulk to the surface which support Senanayake's findings.