Analyzing the effect of pressure on the properties of point defects in *γ*UMo through atomistic simulations

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**Abstract** this is the abstract

# Introduction

Background on UMo fuel

Pressure state on UMo

Atomistic Calculations on UMo summary

What we will do

# Computational Details

Molecular dynamics simulations are performed utilizing the LAMMPS [1] software package and the U-Mo angular dependent potential (ADP) [2]. A 14x14x14 supercell consisting of 5488 atoms is constructed in a body-centered cubic (bcc) structure. Relaxation is performed in an NPT-ensemble, relaxing each x, y, and z component individually, with a damping parameter of 0.1. A Nose-Hoover thermostat is utilized with the damping parameter set to 0.1 ps. Systems are investigated over a range of temperatures, from 600 K up to 1200 K, in increments of 200 K. This temperature range was chosen due to the inherent properties of the potential, in that below 600 K *γ*U becomes mechanically unstable and above 1200 K the crystal structure is approaching the melting point. Systems are relaxed for 100 ps, with volumes averaged over the final 50 ps. The equilibration is performed at a given pressure, ranging from -10 kbar to +10 kbar (-1 GPa to +1 GPa) in increments of 5 kbar. This pressure range should exceed any expected stress state of the fuel, and as such should present the possibilities of extreme behavior on defect evolution. Additionally, trends in behavior can be determined and explored at the pressures of interest. Eight individual compositions are investigated, including bcc U and bcc Mo, U-5Mo, U-10Mo, U-15Mo, U-30Mo, U-50Mo, and U-70Mo. All compositions are given in weight percent unless otherwise noted. This variation in composition allows for analysis for a wide range of U-Mo systems, including all relevant compositions in monolithic fuel.

Following the relaxation, the system is scaled to the averaged volume as determined from the NPT simulation. A relaxation of 50 ps is performed, the final 25 ps of which is utilized to determine average energies. A defect (vacancy or interstitial) is then inserted into the system and allowed to evolve for 50 ps, the final 25 ps of which is utilized to determine average energies. For an alloy composition, a proportional number of atoms are either removed or inserted, depending on the defect type, to closely maintain the stoichiometry of the system. For interstitials, an atom is randomly deposited into the supercell, provided that no other atom is within 1.5 Å, allowing for a random sampling of the entire supercell and all possible local configurational environments. To ensure statistical certainty of the results, 2000 simulations for each defect type, pressure, and temperature are performed.

The formation energy is defined as:

where *n* is the total number of atoms in the system with no defects and or is defined as:

where is the total energy of the system either with or without a defect, is the number of uranium atoms in the system, is the energy per atom of U, is the number of molybdenum atoms in the system, and is the energy per atom of Mo. The energy is defined for a given temperature and pressure, according to the system of interest.

The diffusion coefficient as a function of temperature and pressure is determined for the same sets of pressures as described above, but only for temperatures at 800 K and above. This is due to the limited thermal diffusion at low temperatures on a molecular dynamics time scale. The number of compositions is reduced to five (bcc U, U-5Mo, U-10Mo, U-15Mo, and bcc Mo) due to the computational cost associated with diffusion calculations. However, the primary concentration range of interest for U-Mo monolithic fuel is encompassed by this compositional range. An identical procedure is followed for the implementation of defects for investigation of diffusion as that which was followed for the investigation of defect energies. Following the defect insertion and relaxation, an additional evolution step of 10 ns was performed, over which the mean-squared displacement of the total system, and of each elemental species, was tracked. Over this 10 ns trajectory, three overlapping trajectories were obtained, each of length 6 ns, in order to subsample the trajectory and increase the statistics of the dataset. Additionally, five unique simulations are performed for each temperature, composition, and pressure, to further ensure statistical significance of the results. This results in a standard error for defect energies of less than 0.05 eV.

# Results

## 3.1. Point Defect Formation Energies

An example of the formation energy as a function of pressure for U-10Mo at 1200 K is shown in Figure 1. In correspondence with prior work [3] on defect energetics in U-Mo systems, the interstitial formation energy for the nominal case is less than 1 eV (0.62 eV) and the vacancy formation energy is significantly high than the interstitial formation energy (1.92 eV). Considering slight differences in methodology, this is reasonable agreement with the previous literature. From Figure 1, it can be seen that as vacancies and interstitials exhibit opposite trends as a function of applied pressure, as would be expected. As a crystal structure is compressed (positive pressure), atoms are closer together than in the equilibrium case. As such, it would be expected that a vacancy is more easily formed in the compressive state, and this is indeed observed. In the tensile state (negative pressure), atoms are farther apart than at equilibrium and there is additional space between the atoms. In this case, it would be expected that it is comparatively easier for an interstitial for form, and this is indeed observed. There is a generally linear dependence of the formation energy on the applied pressure in the system, with vacancies exhibiting a negative slope and interstitials exhibiting a positive slope. The total magnitude change in the defect formation energy for this case is 0.14 eV and 0.17 eV for interstitials and vacancies, respectively. This corresponds to approximately a 4-5X higher defect concentration across this pressure range.



Figure . The interstitial and vacancy formation energy as a function of pressure for U-10Mo at 1200 K.

Generalizing to the U-Mo system, the interstitial and vacancy formation energies as a function of composition and pressure at 1200 K are shown in and , respectively. The defect formation energies vary in a similar manner as a function of composition, with a minimum in the formation energy at 20-30 atomic percent. Interestingly, this is the target composition (22 atomic percent) for U-Mo monolithic fuel. Additionally, defect energies are at a maximum for the pure bcc Mo system for both interstitials and vacancies. The pressure sensitivity is not uniform for defect type and composition, in that interstitials are the most sensitive to pressure at intermediate compositions (40-60 atomic percent), while vacancies are the most sensitive to pressure in the U-rich regime. The trends of applied pressure observed in hold for all compositions.



Figure . The interstitial formation energy as a function of composition for five applied pressures at 1200 K.



Figure . The vacancy formation energy as a function of composition for five applied pressures at 1200 K.

The temperature dependence of the nominal pressure defect formation energies is shown in . For interstitials, the temperature dependence undergoes an inflection point as a function of composition, in that in the U-rich regime, higher temperatures lead to higher interstitial energies, while in the Mo-rich regime higher temperatures lead to lower interstitial energies. This transition occurs at approximately 30 atomic percent or 15 weight percent Mo. For vacancies, the trend of defect energy with temperature is consistent across the compositional spectrum, in that higher temperatures lead to higher defect energies. The sensitivity of this temperature dependence varies with composition, with the most temperature-sensitive compositions in the U-rich regime. The application of pressure does affect the temperature dependence of defect formation energies, nor does the temperature affect the trends of applied pressure on defect formation energies. However, it does appear that at lower temperatures, the effects of pressure on interstitial formation energy are slightly dampened. Averaging over the entire compositional regime, an applied pressure of 10(-10) kbar at 1200 K produces a 11(9)% increase(decrease) in the formation energy. At 600 K, an applied pressure of 10(-10) kbar produces a 6(7)% increase(decrease) in the formation energy.



Figure . Temperature and compositional dependence of interstitial and vacancy formation energies in U-Mo.

It is found that generally, vacancies are much less sensitive to pressure than interstitials, and that sensitively is not significantly affected by the temperature of interest. On average, an applied pressure of 10(-10) kbar produces a 3% increase(decrease) in the vacancy formation energy. Since the magnitude of the vacancy formation energy is larger than the magnitude of the interstitial formation energy, the absolute (not relative) change in the defect formation energy with applied pressure is approximately the same for both interstitials and vacancies. Under reasonable applied bulk pressures below the yield point (<100 MPa), negligible deviations in the defect formations are observed. However, in circumstances where the pressures may be quite large, e.g., in the area surrounding a highly pressurized nanometer-sized bubble, statistically significant changes in the local defect formation energy could be observed, potentially altering fission gas bubble evolution and creep behaviors.

## 3.1. Point Defect Diffusion

The diffusion coefficient of interstitials and vacancies as a function of composition and temperature is shown in .



Figure . Diffusion coefficient of interstitials and vacancies as a function of temperature and composition.

The diffusion coefficient for vacancies and interstitials as a function of pressure in U-10Mo at three temperatures is shown in . There is minimal variation as a function of



Figure . Diffusion coefficient of vacancies and interstitials as a function of pressure for U-10 Mo

# Conclusions

# References

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