

Modelling temperature and radiation-induced diffusion in transmutation targets

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Abstract

Introducing transmutation targets in the nuclear fuel cycle calls for a need of new fuel code models to be able to predict the behaviour of such fuels or targets during irradiation. To reach that goal one either has to extend existing models to apply for new irradiation conditions and to include more detailed information on several for actinides or develop completely new models for the purpose. Whichever option one chooses there is a substantial lack of experimental data needed for fuel code purposes. To bridge this gap, first principle calculations can be utilised to estimate desired parameters. Here we present an approach where first principle calculations is used together with rate theories to model diffusion in the inert matrix of cermet and cermet transmutation targets during irradiation.

Introduction

Among the many candidate fuels and targets for transmutation purposes are the ceramic-ceramic (cercer) and ceramic-metallic (cermet) fuels. The former most popularly designed as a magnesium oxide inert matrix enclosing the oxide fuel particles and the later usually designed with a molybdenum inert matrix instead of MgO. In both cases the amount of matrix material varies in between 50-80% depending on application [1]. In transmutation applications the amount of americium and potentially curium in the fuel will cause large production of helium due to alpha decay and effectively create helium gas concentrations much larger than the accumulated fission gas concentration in the fuel. As earlier experiments where spinel was used as the inert matrix material has shown the helium has a potential to severely affect swelling behaviour [2]. In this paper we will therefore present our work to investigate this further for the newer designs of cercer and cermet fuels using *ab initio* methods.

Methods

A model on the atomistic level is needed to fully understand the mechanisms responsible for helium-induced fuel swelling. For this purpose we have chosen to model the inert matrix materials using *ab initio* methods within the framework of density functional theory. The code used for the modelling efforts was VASP 4.6 [3] and throughout the whole process PAW-GGA potentials have been used with a cut-off energy of 500 eV. First defect energies of point defects in the bulk material were calculated using a super cell technique; next helium migration energies were calculated as well as entropy factors for the different realisable He-bulk defects involved in the process.

From these results the jump rate in between different defects can be calculated through [4]:

$$\Gamma = \nu e^{\frac{-\Delta E}{k_B T}}$$

where ΔE is the migration energy in between defect states, ν the frequency pre-factor consisting of the product configurational entropy and the effective vibrational frequency of the jumping atom, k_B the Boltzmann constant and T the absolute temperature. In the case of helium in molybdenum this could be compared with experimental results to verify the theoretical model.

These results can then be introduced in a rate theory, which predicts the concentration of defects in the bulk during irradiation. For such a model to be complete also the diffusion coefficient of several species has to be calculated. This is done from the following relation [5]:

$$D = \alpha C \Gamma$$

where α is the Einstein factor multiplied with appropriate configurational factors, C is the concentration of the species and Γ is as defined above.

Helium in cermet fuel

In the case of the molybdenum matrix the defects formed during helium implantation have been shown to take the form of helium-vacancy clusters here denoted He_nV_m . From these clusters helium atoms are released through thermal activation and form interstitial defects that are very mobile (typical migration energies are calculated to 0.053 eV) in the molybdenum bcc lattice. Since others have performed helium desorption experiments with helium in single crystal molybdenum [6-7], where helium has been implanted in the crystal at different temperatures and the crystal later being heated with a constant heating rate. From this the parameters in the jump rate have been calculated. These results together with our experimental results are shown in Table 1. As can be seen our results agree well with the experiments except for elevated temperatures. This is most likely the result of that vacancy diffusion is not taken into account in the experimental results. Excluding the possibility of substitutional migration of helium atoms in the lattice.

Table 1: Binding energy and effective frequency for the reaction $\text{He}_i\text{V}_j \rightarrow \text{He} + \text{He}_{i-1}\text{V}_j$

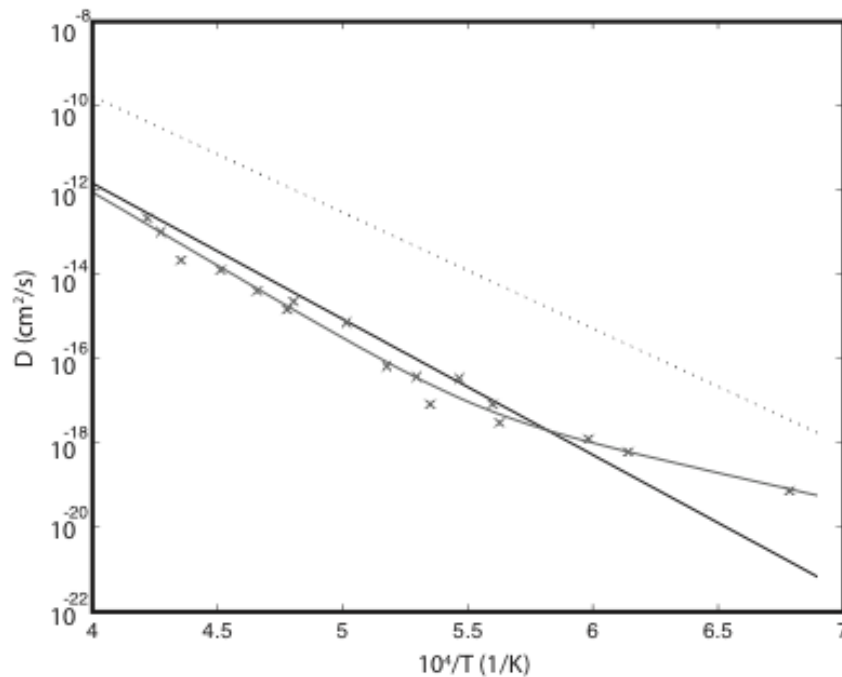
State	ΔE (eV)			ν (s ⁻¹)		
	This work	Ref. [6]	Ref. [7]	This work	Ref. [6]	Ref. [7]
He ₅ V ₁	2.00	2.11	2.32	1.9×10^{13}	0.7×10^{13}	6.2×10^{14}
He ₄ V ₁	2.54	2.4	2.7	1.6×10^{14}	3×10^{13}	5.3×10^{15}
He ₃ V ₁	2.54	2.6	2.61	2.3×10^{13}	5×10^{13}	2.3×10^{14}
He ₂ V ₁	2.67	2.9	2.80	1.9×10^{13}	3.0×10^{14}	1.4×10^{14}
He ₁ V ₁	3.64	3.8	3.75	7.6×10^{13}	5.0×10^{15}	3.0×10^{15}
He ₂ V ₂	3.94	–	–	–	–	–
He ₁ V ₂	3.90	–	–	–	–	–

Helium in cercer fuel

Since MgO is an ionic compound the self-diffusion mechanisms are more complicated than in the case of Mo. We therefore started with investigation the different mechanisms responsible for this. First, the effectively charged vacancies in any ionic compound demand taking charge neutrality into account when estimating concentrations of defects. Second, the strong binding energy of a magnesium and an oxygen vacancy in an uncharged divacancy gives rise to another possible migration mechanism much more uncommon in e.g. metals [8].

Due to charge neutrality the concentration of magnesium and oxygen vacancies more often are controlled by the concentration of trivalent impurities in the material than temperature through thermal activation. Especially when it comes to oxygen migration this effect has been clearly confirmed in diffusion experiments, and divacancy diffusion has been shown to account for most oxygen diffusion in MgO [8]. We have therefore calculated the diffusion coefficient for both divacancy migration and Schottky defect migration and compare these results with experimental results in Figure 1.

Figure 1: Calculated diffusion coefficients for divacancy diffusion of oxygen (solid black line), Schottky defect migration (dotted black line) and experimentally measured diffusion coefficient of oxygen (grey crosses and suggested fit from original paper as grey line) [9]



Conclusions

We have studied helium diffusion in molybdenum and self-diffusion in magnesium oxide. The results agree to a large extent with experimental results indicating that modelling of helium diffusion and more importantly trapping in inert matrices, are possible and can be done through rate theory models. Such models are to be developed and compared with experimental results from in core experiments with these inert matrices.

References

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