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# On the relationship between dynamic solubility, multi-atom bubble nucleation, irradiation-induced re-solution, and the bubble size distribution in Xe implanted Mo

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## INTRODUCTION

U-Mo alloys are candidate fuels for both research and test reactors, as well as for advanced power reactors. A critical requirement for these candidate fuels is stable swelling behavior over their expected lifetime. In-reactor deformation of these materials is primarily driven by irradiation induced swelling where the primary component is fission gas (Xe and Kr) generated by decay of the primary fission products.

An understanding of the behavior of the gas in the material as a function design operating conditions, such as temperature and fission-rate, is greatly leveraged by the development of mechanistic models. Due to the inherent uncertainty of proposed behavioral mechanisms resulting from the unavailability of critical materials properties of the irradiated material, these models require extensive validation. In-reactor experiments and the associated post-irradiation examinations are expensive. In addition, it is very difficult to validate single effect mechanisms from a multivariate environment. For that reason, ion implantation experiments are often used to facilitate the validation process.

However, the interpretation of ion implantation experiments and the mapping of the observed phenomena to an in-reactor environment is complicated by the non-homogeneous nature of the implantation process, thin specimen size that introduces surface effects, as well as operating conditions that are outside the range of in-reactor design specifications. This paper proposes a theoretical foundation as well as a calculation methodology aimed at circumventing these difficulties.

## Ion Irradiation Experiment

Pre-thinned Mo specimens were implanted with 300keV Xe<sup>+</sup> ion beam at the Intermediate Voltage Electron Microscope

(IVEM-Tandem) facility at Argonne. The implantation experiment was carried out at 300 °C. The implantation energy of 300 keV was selected such that the peak of implanted Xe ion is at a depth of about 35-45 nm. As the measurement of the bubble size distribution mostly take place at a thickness of about 60-80 nm, the implantation is believed to have close to maximum Xe ion retention in the specimens. The thickness was estimated with the thickness fringes and the measurement locations were tracked with markers (objects that do not move or change contrast with irradiation) during the entire process of the ion irradiations. Size distributions of Xe bubble features were measured with in situ transmission electron microscopy (TEM). Each measurement (at a specific dose) accumulated 5-10 measured areas for number density measurements and 120-200 measured features for size measurements. Xe bubble measurements were conducted in regions 60-80nm thick.

## Model

A kinetic rate-theory model for the nucleation and evolution of the gas bubble size distribution is applied to the study of noble gases in irradiated Mo. The model is described by the equations of the form:

$$\frac{dc_g}{dt} = \beta_g(t) - 4\pi D_g c_g \sum_i R_i C_i + b \sum_i N_i C_i \quad (1)$$

$$\frac{dN_i}{dt} = 4\pi D_g R_i c_g - b N_i \quad (2)$$

$$\frac{dC_i}{dt} = 0 \quad (3)$$

where  $c_g, D_g$  is the density of gas in solution and the gas-atom diffusion coefficient, respectively;  $C_i, N_i,$  and  $R_i$  represent the density, number of atoms contained within, and radius of gas bubbles in the  $i$ -th size class, respectively; and,  $b$  is the irradiation-induced gas atom re-solution rate from bubbles. In

Eq. (1),  $\beta_g(t)$  is the net ion implantation rate into the specimen where the net is ions implanted minus ions escaping to the surface of the specimen.

A multi-atom gas-bubble nucleation mechanism has been proposed based on the interpretation of measured bubble size distributions wherein once the dynamic solubility of the material has been exceeded bubble nucleation commences [1]. Subsequent nucleation events depend on gas in solution again reaching the solubility limit. This process is hampered by the sink nature of the nucleated bubble distribution: bubbles grow by the accumulation of gas atoms that are diffusing in the material.

The model is based on the following assumptions: 1. A critical value for the amount of gas in solution (the dynamic solubility) exists above which the gas precipitates into bubbles, 2. At nucleation all gas in solution precipitates into bubbles, 3. The bubbles are non-interacting and do not accumulate any additional gas atoms during the relaxation phase, and 3. Subsequently, in order to lower the free energy of the system, the over-pressurized nuclei relax by absorbing vacancies until the bubbles reach equilibrium. The as-nucleated bubble size distribution,  $c_n(r)$ , is obtained by solving the following set of equations:

$$\frac{1}{m(r)} \frac{dm(r)}{dr} = \frac{3}{r} \left( 1 - \frac{rkT}{(3rkT + 2\gamma b_{vdw})} \right) \quad (4)$$

$$\frac{1}{r'(r)} \frac{dr'(r)}{dr} = - \frac{1}{(4/3\pi r'^3 X(r) (\frac{\Omega}{r'} + \frac{kT}{2\gamma}))} \quad (5)$$

$$\frac{dc_n(r)}{dr} = - \frac{1}{m(r)} \frac{dm(r)}{dr} - \frac{3}{r'(r)} \frac{dr'(r)}{dr} \quad (6)$$

where

$$X(r) = \frac{rkT}{(2\gamma(4/3\pi r'^3 - b_{vdw}m(r)))}$$

and  $r'$  and  $r$  are the un-relaxed and relaxed bubble radii, respectively,  $m(r)$  is the number of atoms in a freshly nucleated bubble,  $\Omega$  is the atomic volume,  $k$  is Boltzmann's constant,  $\gamma$  the surface energy,  $b_{vdw}$  is the Van der Waals constant, and  $c_n(r=rg) = C_s$ , where  $rg$  is the radius of an Xe atom and  $C_s$  is the dynamic solubility limit.

Examining the steady-state solution of Eq. (1) and (2), one consequence of this

nucleation mechanism occurring in a low-temperature environment where the gas bubbles are immobile, and where gas-atom re-resolution from bubbles is operative is that the as nucleated bubble-size distribution evolves toward a very narrow mono-modal shape.

Xe diffusion is assumed to be irradiation enhanced at the relatively low temperature of the Xe implantation in Mo. MD studies have indicated that there is very limited cascade melting from the 300 KeV Xe ions, and as such the mobility enhancement comes from irradiation-produced defects. Following the standard derivation of irradiation-enhanced self-diffusion in the recombination regime [2], the Xe diffusion coefficient has the form

$$D_g = \xi(T)G \quad (7)$$

where  $G$  is the ion implantation rate, and where  $\xi(T=573 K) = ?$

The dynamic solubility and the re-resolution rate are a function of damage rate and projectile energy. MD simulations have indicated that irradiation induced re-resolution of Xe bubbles primarily occurs for ions having energy  $< 1$  KeV. As such, the gas-atom re-resolution rate has the form

$$b(l) = \mu_{E1(l)} b_0 G \quad (8)$$

where  $\mu_{E1(l)}$  is the fraction of ions at a distance  $l$  into the specimen having energy less than 1 KeV, and  $b_0$  is a constant.

In an analogy with the irradiation-induced re-resolution process, where gas atoms are ejected back into solution due to energy transfer between the ion projectile and the bubble, the concept of dynamic solubility can be viewed as the re-resolution process running in reverse. In this case, the energy transfer between the ion projectile and a "cloud" of gas atoms hinders the condensation of the cloud into a solid precipitate. Only when the local concentration of gas atoms is larger than a critical value, will this metastable state be left behind and the free energy of the system lowered by the subsequent formation of a solid bubble precipitate. As such, it is here assumed that the dynamic solubility has a similar dependence as Eq. (8), i.e.

$$C_s(l) = \mu_{E1(l)} C_{s0} G \quad (9)$$

where  $C_{s0}$  is a constant.

In order to capture the effect of the dependence of projectile energy on the ion penetration depth, the specimen was divided into 10 equal width regions and the ion energy spectrum and net ion implantation rate were estimated using the SRIM [3] code as a function of distance from the front specimen surface.

## RESULTS

Calculations of the bubble size distribution made with the theoretic model for the ion-irradiation experiment described above are compared with the measured distribution at an ion dose of  $1.5 \times 10^{16}$  ions  $\text{cm}^{-2}$  in Figure 1. Figure 1 was generated using Eq. (1)-(9) by the superposition of approximately mono-modal bubble-size distributions whose density and size are dependent on the depth into the specimen. The results shown in Fig. (1) demonstrate that the physics and methodology presented in this paper provide a reasonable interpretation of the observations.

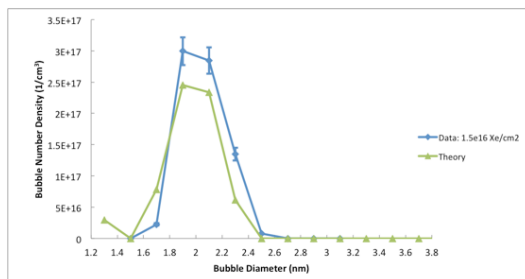


Figure 1. Calculations of the bubble size distribution made with the theoretic model for the Xe ion-implantation experiment compared with the measured distribution

## CONCLUSION

In-reactor irradiation of U-10Mo occurs in a relatively homogeneous and isotropic fashion. As such, application of the model presented in this paper would predict a relatively monomodal size distribution of the

Xe and Kr bubbles nucleated in the bulk. In fact, TEM observations [4] confirm this picture by the appearance of a superlattice of gas bubbles having relatively uniform diameter and spacing of about 2 and 7 nm, respectively. The gas-bubble size distribution shown in Fig. 1 is due to the non-homogeneous, non-isotropic nature of the ion implantation process that leads to a depth dependence of both the irradiation induced re-resolution rate and the dynamic solubility limit. It is clear from this analysis that any attempt to interpret the measured bubble-size distribution shown in Fig. 1 without due consideration of the non-homogeneous, non-isotropic nature of the irradiation will lead to incorrect interpretation of the underlying physics.

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